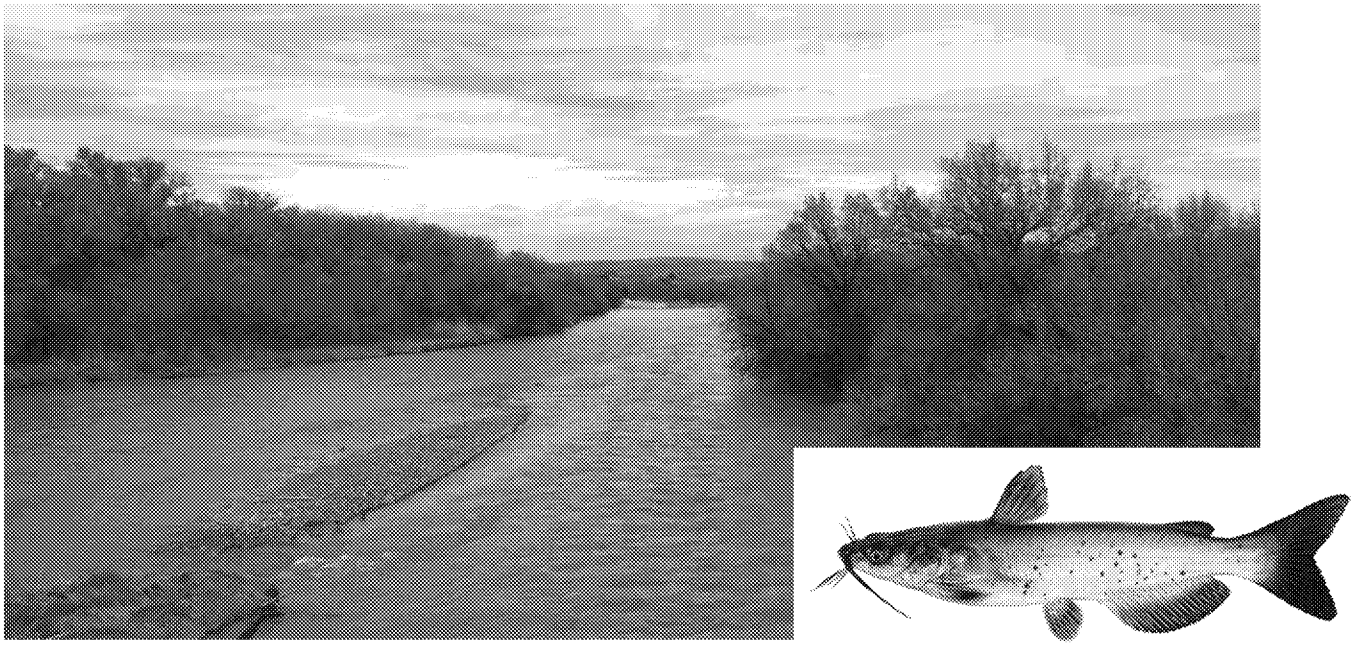
Quality Assurance Project Plan

Sample Preparation and Analysis Activities for the San Juan River Fish Tissue Contaminant Study

(Volume 2 of 2)

Document Control Number 481



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This quality assurance project plan (QAPP) has been prepared according to guidance provided in EPA Requirements for Quality Assurance Project Plans (EPA QA/R-5, EPA/240/B-01/003, U.S. Environmental Protection Agency, Office of Environmental Information, Washington, DC, March 2001) to ensure that environmental and related data are collected, compiled, and/or generated for this project are complete, accurate, and of the type, quantity, and quality required for their intended use. Tetra Tech will conduct work in conformance with the quality assurance program described in the quality management plan for Tetra Tech's Fairfax Group and with the procedures detailed in this QAPP.

Group A: Project Management Elements

A1. APPROVAL SHEET

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Project Manager
USEPA Region 9

Eugenia McNaughton 6/1/17 — Date
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Tara Cohen 5/24/2017 — Date
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A4. PROJECT/TASK ORGANIZATION

This is Revision 0 of the Quality Assurance Project Plan (QAPP) that describes the quality assurance (QA) and quality control (QC) activities and procedures to be used while preparing and analyzing samples for the Navajo Nation Environmental Protection Agency's San Juan River Fish Tissue Contaminant Study (hereafter referred to as the San Juan River Fish Tissue Study) during April through September of 2017. This QAPP (Volume 2 of 2) presents the methods and procedures that will be used for the preparation and analysis of fish tissue from pre-selected sites on the San Juan River, and the QA procedures that will be employed. It was prepared according to guidance found in *EPA Requirements for Quality Assurance Project Plans* (USEPA 2001). Tetra Tech (2017) prepared a Volume 1 of 2 QAPP to address the sample collection effort for this study; this QAPP was approved by the Navajo Nation Environmental Protection Agency (NNEPA) Project Manager (PM)/QA Officer and the U.S. Environmental Protection Agency (EPA) Region 9 PM and QA Officer.

The organization of our project team provides the framework for sample preparation and analysis to meet the study objectives. This framework will facilitate project performance and adherence to QC procedures and QA requirements. Key roles are filled by the staff responsible for the generation of valid data and for routinely assessing the data for precision and accuracy, as well as the persons responsible for approving and accepting final products and deliverables. The project and QA personnel include staff from the NNEPA, the U.S. EPA Region 9, Tetra Tech, and TestAmerica Laboratories, Inc. (TestAmerica). The project organizational diagram is presented in Figure 1, and includes relationships and lines of communication among key project team members.

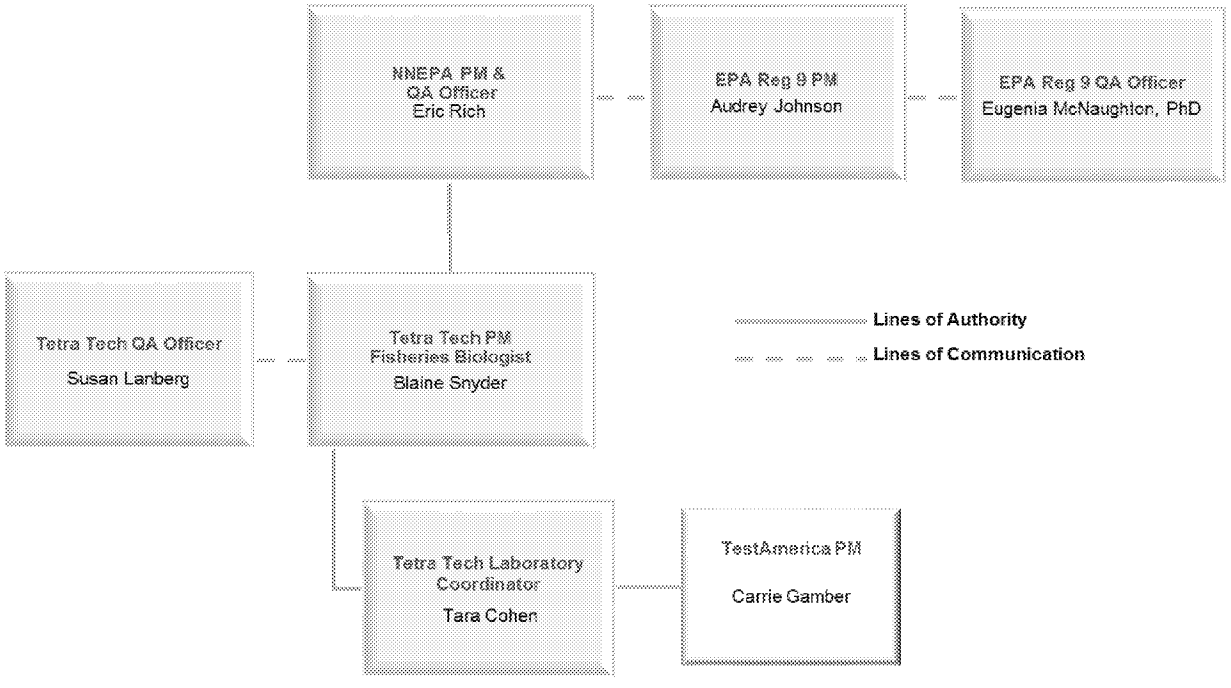

Figure 1: Organizational Diagram

The **NNEPA PM** is **Eric Rich**. As PM he will provide oversight for all study activities, and adherence to design objectives. He will review and approve the QAPP, fish sample preparation standard operating procedures (SOPs) (refer to Appendix A), and other materials developed to support the project. He will coordinate with Tetra Tech and NNEPA staff to ensure technical quality and contract adherence. He will also serve as the **NNEPA QA Officer.** In this role, he will conduct external performance and system audits of the procedures, and participate in QA reviews of the study.

The **EPA Region 9 PM** is **Audrey Johnson**. As PM she will coordinate with NNEPA staff to ensure technical quality. She will review and approve the QAPP, SOPs, and other materials developed to support the project. The **EPA Region 9 QA Officer** is **Eugenia McNaughton, PhD**, who will be responsible for reviewing and approving the QAPP. She will also review and evaluate laboratory procedures, and participate in QA reviews of the study, as appropriate.

The **Tetra Tech PM** is **Blaine Snyder**, who will coordinate all project assignments, and provide oversight for all study activities and adherence to design objectives. He will review and approve the QAPP, SOPs, and other materials developed to support the project. He will provide support to the NNEPA in interacting with the project team to ensure technical quality requirements are met in accordance with project design objectives. He will implement corrective actions and provide professional advice to staff. He will also oversee all sample preparation activities at the Tetra Tech Biological Research Facility in Baltimore, Maryland, and manage the analytical laboratory subcontract with TestAmerica. The **Tetra Tech Laboratory Coordinator** is **Tara Cohen**, who will facilitate and track the sample preparation activities. She will also track the activities and progress of the analytical laboratory. The **Tetra Tech QA Officer** (QAO) is **Susan Lanberg**, who will provide support to the NNEPA and the Tetra Tech PM in preparation of the QAPP and SOPs. She will approve the QAPP and monitor QC activities to determine conformance.

The **TestAmerica PM** is **Carrie Gamber**. As PM, and under subcontract to Tetra Tech, she will be responsible for managing all aspects of the technical support related to sample analysis and analytical data deliverables. She will coordinate with Tetra Tech to ensure that samples are analyzed on time and in accordance with this QAPP, and that the data deliverable is prepared according to the TestAmerica Quality Assurance (QA) Manual.

The **TestAmerica QAO** is **Virginia Zusman**. As QAO, she will be responsible for providing necessary performance data to develop this plan (reporting and quantitation limits and laboratory acceptance criteria for control samples, SOPs, and relevant quality documentation), overseeing adherence to laboratory quality policy and procedures, initiating corrective actions, and verifying effectiveness of corrective actions. She will support the laboratory PM in addressing technical and quality-related inquiries and overseeing the final review of laboratory reports and deliverables. She will also assist the PM in coordinating with Tetra Tech to ensure that samples are analyzed on time and in accordance with this QAPP, and that the data deliverable is prepared according to the TestAmerica QA Manual.

A5. PROBLEM DEFINITION/BACKGROUND

On August 5, 2015, EPA conducted a study of the Gold King Mine (GKM) near Silverton, Colorado to evaluate water releases from the mine and assess the viability of additional mine remediation (USEPA 2016). During excavation activities, pressurized water began leaking, spilling about three million gallons of water into Cement Creek, a tributary of the Animas River. The Animas River originates in the mountain

peaks of San Juan County, Colorado, and ends in Farmington, New Mexico, where it flows into the San Juan River.

EPA's initial monitoring efforts began in the fall of 2015 and continued through the fall of 2016. This monitoring effort focused on identifying changes in water quality, sediment, and biological condition since the GKM release in an effort to characterize the potential impacts of this event. EPA began engaging with State and Tribal partners during this time to discuss expanding the monitoring to better focus on the concerns of local stakeholders in their jurisdictions. This monitoring effort would focus on assessing the condition of sites downstream of the GKM release as compared to water quality standards and sediment risk benchmarks (USEPA 2016).

A6. PROJECT/TASK DESCRIPTION

Tetra Tech will conduct a fish tissue contaminant study in the San Juan River for the NNEPA. The focus will be on prevailing human health risk associated with fish consumption subsequent to the GKM spill, and will be based on monitoring current contaminant levels in fish (specifically metals relevant to the GKM spill).

Task 1: Mobilization

Mobilization tasks include all activities that must be completed prior to the San Juan River fish tissue sampling event. The Tetra Tech PM has worked with the NNEPA PM to finalize the study design and lay out a timeline for tasks and deliverables. Tetra Tech has communicated and coordinated with the NNEPA PM to confirm the five San Juan River sampling locations, lay out the logistical plan for sampling, and schedule the work. Tetra Tech coordinated with the NNEPA PM to prepare and secure approval of the Sample Collection Activities QAPP (Volume 1 of 2) on March 14, 2017. Tetra Tech will coordinate with the NNEPA PM to prepare and secure approval of the Analytical Activities QAPP (Volume 2 of 2). Tetra Tech set up a subcontract agreement with TestAmerica to serve as the supporting analytical chemistry laboratory. The Tetra Tech PM has coordinated with the NNEPA PM and the TestAmerica PM to identify preferred analytical methods. Tetra Tech will also purchase the supplies for laboratory processing (e.g., sample homogenate containers) and shipment of the fish sample aliquots.

Task 2: Implementation

Implementation tasks include all activities associated with sample collection and distribution to the sample preparation laboratory. Tetra Tech will provide one senior fisheries scientist to be on site during a single, 6-day sampling event conducted by the Navajo Nation Department of Fish and Wildlife (NNDFW) personnel. The Tetra Tech and NNDFW Field Team will collect fish from five river locations between Farmington, New Mexico and Bluff, Utah, focusing on populated areas in the reach. Sampling location specifics are provided in the Sample Collection Activities QAPP (Volume 1 of 2) (Tetra Tech 2017). The Field Team will attempt to collect two composites (i.e., replicate samples) of five fish each from each of the five sampling sites (following the recommendations and methods in EPA's Fish Consumption Advisory Guidance documents, USEPA 2000a and 2000b) focusing on fishes that are commonly consumed by humans. Every attempt will be made to collect the desired number and species of fish targeted for study, but the success of the sampling effort will ultimately depend on the natural diversity and abundance fish

at each location. The Tetra Tech fisheries biologist will coordinate the sample collection and select target species/specimens. The Tetra Tech biologist will wrap, label, and freeze all fish as whole specimens and ship all fish samples via priority overnight shipping service to the Tetra Tech Biological Research Facility in Baltimore, Maryland.

On receipt in Baltimore, Tetra Tech will implement the QC activities and procedures described in the approved QAPP (Tetra Tech 2017) and Appendix A to prepare (i.e., fillet and homogenize) samples for subsequent analysis including requisite inspection and verification of sample integrity, reconciliation of any sample condition or identification issues, as required, and procedural controls.

Procedural controls and sample homogenates will be transferred to the analytical laboratory under custody. Tetra Tech will verify that samples are received intact in the laboratory, resolve any sample identification inconsistencies as a result of condition on receipt, and respond to project-specific technical inquiries from the laboratory during the performance of the analytical laboratory subcontract task.

Following analysis and upon receipt of the laboratory data package, Tetra Tech will verify completeness and compliance of the report relative to the requirements of the respective project planning documents, including this plan.

Tetra Tech will prepare the final report, including summarized sample results with comparison to appropriate criteria. Tetra Tech's report will also document all departures from the approved project plans, describe apparent limitations, and assess their impact on the usability of the data for the current project and future data users.

Task 3: Analysis

Analysis tasks include all activities associated with sample preparation and chemical analysis. To summarize, Tetra Tech will fillet, composite, homogenize, label, and freeze all fish samples at the Baltimore, Maryland Biological Research Facility. Aliquots of frozen tissue homogenates will be shipped to TestAmerica via a priority overnight shipping service (e.g., FedEx). Tetra Tech will store extra (archive) tissue at our Biological Research Facility (for possible future analysis or eventual delivery to the NNEPA). TestAmerica will analyze each composite sample for the following suite of metals: aluminum, antimony, arsenic, barium, beryllium, calcium, cadmium, chromium, cobalt, copper, iron, lead, magnesium, manganese, mercury, molybdenum, nickel, potassium, selenium, silver, sodium, strontium, thallium, vanadium, and zinc (wet weight). The lab will prepare electronic and hard copy analytical data deliverables. Tetra Tech will conduct data validation of the analytical results.

Task 4: Reporting

Reporting tasks include all activities associated with documenting sampling and analysis results. Tetra Tech will prepare a technical report summarizing sampling activities and results, analytical results, and fish tissue metal concentrations in relation to human health protection endpoints. The final deliverable will be a single, comprehensive study document.

A7. QUALITY OBJECTIVES AND CRITERIA

Data of known and documented quality are essential to the success of this monitoring program. Data quality objectives (DQOs) are qualitative and quantitative statements that clarify the intended use of the data, and specify the data quality needed to support specific decisions. DQOs define the type of data needed, identify the conditions under which the data should be collected, and specify tolerable limits on the probability of making a decision error due to uncertainty in the data.

DQO Process

As outlined in *Guidance on Systematic Planning Using the Data Quality Objectives Process* (USEPA 2006a), EPA has developed a seven-step process to establish performance or acceptance criteria, which serves as the basis for designing a plan for collecting data of sufficient quality and quantity to support the goals of a study. Each step of the process identifies criteria that will be used to determine the final study design (USEPA 2006a). The seven-step process for the San Juan River Fish Tissue Study is presented below.

Step 1. State the Problem

This monitoring effort focuses on assessing the San Juan River reach downstream of the GKM release as compared to fish consumption limits based on human health benchmarks. The study will focus on prevailing human health risk associated with fish consumption subsequent to the GKM spill, and will be based on monitoring current contaminant levels in fish (specifically metals). The study goals were defined by NNEPA and NNDFW, and the study design was refined and finalized in collaboration with U.S. Fish and Wildlife Service (USFWS) and Tetra Tech. The schedule was determined based on NNDFW and USFWS expertise regarding optimal times for sampling. The schedule accounts for preferred temperatures and flows for sampling efficiency, and avoids sampling during the spawning season of federally endangered and state protected Razorback Suckers (*Xyrauchen texanus*). There is a fixed budget for this project, which constrained the number of sites, samples, and analyses. The study was designed to fit these constraints while addressing study goals.

Step 2. Identify the Goal of the Study

The goal of the San Juan River Fish Tissue Study is to provide a screening level assessment to help identify the prevailing human health risk associated with fish consumption subsequent to the GKM spill, and will be based on monitoring current contaminant levels in fish (specifically metals relevant to the GKM spill). Additionally, the list of analytes has been expanded to include metals which do not have comparative human health criteria in order to have a baseline and more expansive understanding of metals accumulated in fish tissue. The study seeks to answer the questions:

1. Which metals related to the GKM spill are bioaccumulating in fish tissue?
2. What are the concentrations of metals in fish fillet tissue?
3. How do these concentrations compare to human health screening values (when available)?

Step 3. Identify Information Inputs

In order to answer the San Juan River Fish Tissue Study questions, chemical analysis of selected metals in fish fillet tissue is required. Fillet tissue (rather than whole body samples) will be analyzed to best represent the prevailing human health risk associated with fish consumption. Fish fillet tissue concentrations will be compared to risk-based consumption limits for carcinogenic and chronic health endpoints for the general adult population for target chemicals for which those limits have been established by EPA (EPA 2000b).

Step 4. Define the Boundaries of the Study

The target population for the San Juan River Fish Tissue Study is the population of fish residing or moving through the San Juan River between Farmington, New Mexico and Bluff, Utah, that are commonly consumed by humans. A total of five locations will be sampled within the project boundaries. The sites were selected based on NNEPA, NNDFW, and USFWS expertise and recommendations to best represent areas of the San Juan River that are accessible and commonly fished, areas likely to produce valid samples, and areas within proximity to population centers along river reach.

Temporally, the schedule was determined based on NNDFW and USFWS expertise regarding optimal times for sampling. The schedule accounts for preferred temperatures and flows for sampling efficiency, and avoids sampling during the spawning season of federally endangered and state protected Razorback Suckers (*Xyrauchen texanus*). The primary target species for the San Juan River Fish Tissue Study is Channel Catfish (*Ictalurus punctatus*). Every effort will be made to collect the target species and number of fish; however, the outcome of field sampling efforts will ultimately depend on the natural diversity and abundance of fish at the sampling sites.

Step 5. Develop the Analytic Approach

The fish fillet tissue samples will be analyzed for the suite of metals listed in Table 1, using EPA Method 6020A for 24 metals and Method 7471B for mercury. All of the metals except calcium, magnesium, and potassium were analyzed in EPA's initial work after the GKM spill; the results are included in EPA's January 2017 report *Analysis of the Transport and Fate of Metals Released from the Gold King Mine in the Animas and San Juan Rivers*. Calcium, magnesium, and potassium are part of the analytical method suite, and results will be included at no additional cost. Application of human health thresholds will identify tissue concentrations above a level protective of human health. The fish tissue metal concentrations will be compared to existing EPA risk-based fish consumption limits (EPA 2000b). Tables 2 – 4 present the risk-based consumption limits for three of those metals, i.e., arsenic, cadmium, and selenium. The screening value to be applied for mercury will be the EPA fish tissue criterion for methylmercury (USEPA 2006b). Freshwater fish contamination studies have shown that methylmercury can account for (on average) more than 90% of the mercury concentration in predator fish tissue. USEPA (2000a) and USEPA (2006b) recommended monitoring for total mercury (as planned for the San Juan River Fish Tissue Study) rather than methylmercury in fish contaminant screening studies, applying the conservative assumption that all mercury is present in fish tissue as methylmercury.

Table 1: San Juan River Fish Tissue Study Analytes (using EPA Methods 6020A and 7471B)

Analyte	Included in the 2017 EPA GKM Report?	EPA Risk-based Consumption Limit?	Method Reporting Limit (mg/Kg)	Method Detection Limit (mg/Kg)	Evaluation Benchmarks
Aluminum	Yes		3.00	1.82	
Antimony	Yes		0.200	0.0325	
Arsenic	Yes	Yes	0.100	0.0203	See Table 2
Barium	Yes		1.00	0.0474	
Beryllium	Yes		0.100	0.0243	
Calcium			50.0	8.03	
Cadmium	Yes	Yes	0.100	0.0105	See Table 3
Chromium	Yes		0.200	0.0816	
Cobalt	Yes		0.0500	0.00820	
Copper	Yes		0.200	0.122	
Iron	Yes		5.00	3.68	
Lead	Yes		0.100	0.0481	
Magnesium			50.0	3.33	
Manganese	Yes		0.500	0.174	
Mercury	Yes	Yes*	0.0330	0.00739	0.3 mg/Kg fish tissue based Water Quality Criterion (USEPA 2006b)
Molybdenum	Yes		0.500	0.0784	
Nickel	Yes		0.100	0.0294	
Potassium			50.0	5.35	
Selenium	Yes	Yes	0.500	0.122	See Table 4
Silver	Yes		0.100	0.0133	
Sodium	Yes		50.0	21.1	
Strontium	Yes		0.500	0.0344	
Thallium	Yes		0.100	0.00390	
Vanadium	Yes		0.100	0.0565	
Zinc	Yes		0.500	0.288	

* as Methylmercury

Table 2: Monthly Fish Consumption Limits for Carcinogenic and Noncarcinogenic Health Endpoints – Arsenic (inorganic) (USEPA 2000b)

Risk Based Consumption Limit[a]	Noncancer Health Endpoints[b]	Cancer Health Endpoints[c]
Fish Meals/Month	**Concentrations *(ppm, wet weight)***	**Concentrations *(ppm, wet weight)***
Unrestricted (>16)	0 - 0.088	0 - 0.002
16	>0.088 - 0.18	>0.002 - 0.0039
12	>0.18 - 0.23	>0.0039 - 0.0052
8	>0.23 - 0.35	>0.0052 - 0.0078
4	>0.35 - 0.7	>0.0078 - 0.016
3	>0.7 - 0.94	>0.016 - 0.021
2	>0.94 - 1.4	>0.021 - 0.031
1	>1.4 - 2.8	>0.031 - 0.063
0.5	>2.8 - 5.6	>0.063 - 0.13
None (<0.5)	>5.6	>0.13

a The assumed meal size is 8 oz (0.227 kg).
b Chronic, systemic effects.
c Cancer values represent tissue concentrations at a 1 in 100,000 risk level.

Table 3: Monthly Fish Consumption Limits for Noncarcinogenic Health Endpoint – Cadmium (USEPA 2000b)

Risk Based Consumption Limit[a]	Noncancer Health Endpoints[b]
Fish Meals/Month	**Fish Tissue Concentrations *(ppm, wet weight)***
Unrestricted (>16)	0 - 0.088
16	>0.088 - 0.18
12	>0.18 - 0.23
8	>0.23 - 0.35
4	>0.35 - 0.7
3	>0.7 - 0.94
2	>0.94 - 1.4
1	>1.4 - 2.8
0.5	>2.8 - 5.6
None (<0.5)	>5.6

a The assumed meal size is 8 oz (0.227 kg)..
b Chronic, systemic effects.

Table 4: Monthly Fish Consumption Limits for Noncarcinogenic Health Endpoint – Selenium (USEPA 2000b)

Risk Based Consumption Limit[a]	Noncancer Health Endpoints[b]
Fish Meals/Month	**Fish Tissue Concentrations, *(ppm, wet weight)***
Unrestricted (>16)	0 - 0.029
16	>0.029 - 0.059
12	>0.059 - 0.078
8	>0.078 - 0.12
4	>0.12 - 0.23
3	>0.23 - 0.31
2	>0.31 - 0.47
1	>0.47 - 0.94
0.5	>0.94 - 1.9
None (<0.5)	>1.9

a The assumed meal size is 8 oz (0.227 kg).
b Chronic, systemic effects.

Analytical method selection was based on direct comparison to method applications from previous EPA San Juan River studies. The methods selected are well-documented and widely accessible in commercial laboratories nationally. It should be noted that reporting and detection levels may be variable between laboratories, depending on the market that the laboratory serves. For instance, in considering two laboratories for the same ICP/MS measurement for this study (one mixed waste laboratory and one which supports primarily risk-based client analyses), a factor of 10 was observed between reporting levels (RLs), and a factor of 20 between empirically derived method detection limit (MDL) study results. For the purposes of this data collection, it is acknowledged that reporting limits may not always compare favorably to some of the fish tissue consumption limits. Thus, direct comparison of reported limits or estimated concentrations to human health screening values must be undertaken carefully. Another useful comparison may be tissue concentrations compared to background levels observed in other studies in the area prior to the GKM release, or to data collected by EPA for national probabilistic fish tissue surveys. Samples with no evidence of target elements will be reported as not detected (ND or U) with the laboratory reporting limit. Due to these common reporting conventions, an undetected sample result may appear to suggest a higher concentration than a trace level value observed between the laboratory-derived MDL and RL. The MDL is an empirically determined quantitation limit with a 99% confidence that the value is not zero. Reporting a detection when there is no substance present is known as a "false positive." The EPA MDL is designed to control against false positives at the 99-percent confidence level. Reporting the detection of a substance at the MDL concentration in a blank sample or a sample that does not contain the analyte should be rare (less than or equal to 1 percent). However, the concentration reported is estimated and precision and bias cannot be assumed. Data users are cautioned in the direct comparison of results, despite the range of study elements incorporated into the study design that are intended to limit decision errors (See DQO Step 6 discussion below).

Step 6. Specify Performance or Acceptance Criteria

As described in EPA DQO guidance, a decision error occurs when the data mislead the site manager into choosing the wrong response action. The possibility of a decision error exists because of inherent variability in the data. The two types of decision errors are classified as a false rejection error (Type 1) and a false acceptance error (Type 2), for example, deciding that the baseline condition is false when it is true, or deciding that the baseline condition is true when it is really false. The baseline condition is called the null hypothesis (H_0), for example, the fish are safe to consume. Decision errors, in the context of environmental data collection, are largely controlled in the study design. The collection of sufficient number and types of samples (e.g., in this case to reasonably predict the likelihood of exceeding a human health benchmark) are the primary means to limit decision errors. In the current study, fish (fillets) were selected as a more conservative indicator of risk, as they are less subject to variability associated with conventional water and sediment sampling. In the case of this study design, fish samples were targeted from multiple locations along the San Juan River with locations selected based on access availability and/or actual angler use of the river segments. Species selection favored fishes that are more likely to be consumed by anglers and that are San Juan River resident species (although recognizing that fish may not remain within a specific limited geographical distribution in the river), and to further ensure representativeness the study design calls for the collection of multiple (two) fish composite samples from multiple river segments. Each of the ten samples targeted by the study design will consist of multiple (five) individual adult fish per composite that are similar in length (i.e., length of the smallest specimen in

the composite is at least 75% of the length of the largest individual). Fillets from both sides of all five fish will be removed (i.e., a total of 10 fillets per composite) and homogenized to prepare one composite fillet sample. These design parameters have been applied in national-, regional-, and reach-scale studies for decades, and have been accepted by the scientific community as a valid approach to assessing human health risk.

The goal for sampling completeness is 95%, which recognizes that a few samples sent from the field may not arrive in acceptable condition for inclusion in the study. The overall quality objective for the preparation of the fish fillet samples is to obtain a complete set of samples for each chemical. Analytical completeness is defined as the percentage of valid samples collected in the study for which usable analytical results are produced. The goal for analytical completeness is 95%; it is calculated at the sample-analyte level, such that an issue with the quality of one analyte does not invalidate the entire sample. Please see the *Measurement Performance Criteria* section below for more information.

Measurement control and performance metrics are described for both sample preparation and analysis. Negative controls (blank analyses) will be generated and evaluated in performance of both processing and analysis methods. The negative control for sample processing is the procedural blank (rinsate) generated during homogenization operations. Specific criteria for sample preparation controls are included in the appropriate SOPs. Analytical acceptance criteria for positive (analysis of standard reference materials or spiked control samples) and negative controls (calibration, method and instrument blanks) are described in laboratory SOPs and the QA Manual, and are briefly discussed in Section B5 of this plan. In general, negative controls ideally yield no target analyte values in excess of laboratory-specific method detection limits, but, due to the ubiquitous nature of some elements in the laboratory setting, blank limits are frequently established at the reporting limit. For positive controls, spiked and control sample recoveries in a range of 85-115% are generally considered acceptable for solid matrices.

Step 7. Develop the Plan for Obtaining Data

Tetra Tech, in collaboration with EPA Region 9, NNEPA, NNDFW, and USFWS defined study boundaries, stations, and a projected schedule for the study including consideration of available historical data, the current study questions, and the potential presence of federally protected species in the study area. The plan for obtaining data was presented in a separate approved QAPP (Tetra Tech 2017) describing monitoring design and sample collection. Tetra Tech continues to collaborate with the analytical laboratory to ensure preparedness and optimize the data collection for the current study.

Tetra Tech will provide one senior fisheries scientist to be on site during a single, 6-day sampling event conducted by NNDFW personnel. The Tetra Tech and NNDFW Field Team will collect fish from five river locations between Farmington, New Mexico and Bluff, Utah, focusing on populated areas in the reach. The Field Team will attempt to collect two composites (e.g., five fish each) from each of the five sampling sites focusing on fishes that are commonly consumed by humans. The Tetra Tech fisheries biologist will wrap, label, and freeze all fish as whole specimens and ship all fish samples via priority overnight shipping service to the Tetra Tech Biological Research Facility in Baltimore, Maryland.

Tetra Tech will fillet, composite, homogenize, label, and freeze all composite fish samples at the Baltimore, Maryland Biological Research Facility. Aliquots of frozen tissue homogenates will be shipped to TestAmerica, who will analyze each composite sample for the suite of metals listed in Table 1. The analytical laboratory will prepare electronic and hard copy analytical data deliverables. Tetra Tech will conduct a detailed assessment of the quality of the analytical results, and apply data qualifications as may be appropriate in light of field and laboratory QC results.

Measurement Performance Criteria

Measurement performance criteria are quantitative statistics that are used to interpret the degree of acceptability or utility of the data to the user. These criteria are explained below.

Precision

Precision is defined as the degree of reproducibility of measurements under a given set of analytical conditions. Precision is documented on the basis of replicate analysis, i.e., field replicates, and laboratory duplicate or matrix spike and matrix spike duplicate (MS/MSD) samples. The laboratory objective for precision is to meet the performance for precision demonstrated for the methods on similar samples. Precision for laboratory analyses of samples will be evaluated through laboratory reporting of relative percent differences (RPDs) in duplicate sample analyses, and project staff developing precision estimates for field replicates using the same approach. Relative percent difference (RPD) is calculated as follows:

$$RPD = \frac{|C_1 - C_2|}{\overline{(C_1, C_2)}} \times 100\%$$

where C_1 is the first of two measurements and C_2 is the second of 2 measurements. The absolute difference of the two values is divided by the mean.

$$RPD = \frac{|C_1 - C_2|}{(C_1 + C_2)/2} x100\%$$

where C_1 is the first of two measurements and C_2 is the second of 2 measurements.

Refer to Section B5 of this plan, and the procedure-specific SOPs for laboratory acceptance values and corrective action requirements.

In general, precision of laboratory analyses will be assessed by performing duplicate analyses on at least 5 percent of all media/matrix samples (one per twenty samples) submitted to the laboratory for the program. As the current program includes collection of replicate samples at every station, field precision will be demonstrated in the analyses of those replicates. It should be noted that precision is impacted by sample concentration, and some sample concentrations may be below or near laboratory quantitation (detection and reporting) limits. For this reason, for comparing field and laboratory duplicate analyses, acceptance criteria should include consideration of sample-native concentration. Thus, a reasonable DQO may state that RPD should be ≤ 20 percent when measured concentrations are > 10x the reporting limit, ≤ 50 percent when measurements are ≤ 10x but >2x the reporting limit, and ≤ 100 percent when values

are ≤ 2x the reporting limit. Incorporation of the sample concentration into assessment of duplicate precision affords a more meaningful evaluation than strict assignment of an acceptance limit.

The precision goal will be satisfied by using experienced laboratory technicians to ensure that the samples are processed according to the methods, strictly following both laboratory and method-specific QA specifications.

Accuracy

Accuracy is defined as the degree of agreement between an observed value and an accepted reference or *true* value. Accuracy is a combination of random error (precision) and systematic error (bias), which are due to sampling and analytical operations. Bias is the systematic distortion of a measurement process that causes errors in one direction so that the expected sample measurement is always greater or lesser to the same degree than the sample's true value. EPA now recommends that the term accuracy not be used and that precision and bias be used instead. Because the "true" value of a field sample cannot be known, the primary tool for assessing bias in laboratory analyses is the percent recovery calculation for standard reference materials or LCSs, supported by recovery data measured and reported for spiked field samples. In addition to the systematic error demonstrated by positive controls, matrix spiked samples (MSs) reveal interferences native to the sample matrix, and assist in the overall estimate of bias for study samples for consideration in light of the estimates indicated in the analysis of reference materials. As matrix spikes demonstrate the effects of co-extractable, non-target materials along with the analytical spikes, their recoveries are not as predictable and are not generally used to control the method, but to estimate bias due to matrix. In general, LCS recoveries within 85-115% are considered acceptable for metals analysis. Acceptance criteria for commercially prepared standard reference materials should be based on the certified range accompanying the material (whether in % recovery or absolute concentration range). Percent recovery for control samples or standard reference materials are calculated as follows:

$$\%R = \frac{analytical\,result}{truevalue} \times 100\%$$

Where the *analytical result* is the measured concentration, and the *true value* is the spiked/expected concentration.

Percent recovery for MS or MSD sample analyses are calculated as follows:

$$\%R = \frac{(spikedsampleresult - sampleresult)}{amountspiked} \times 100\%$$

Where *spikedsampleresult* = the concentration measured in the MS or MSD sample, *sampleresult* is the measured concentration in the unspiked sample, and *amountspiked* is the effective final spike concentration added to the MS/MSD samples. Generally speaking, for the analysis of metals in solid samples are considered valid if control and MS recoveries are within 80-120 percent.

The accuracy goal will be satisfied by using experienced laboratory technicians to ensure that the samples are processed according to the methods, strictly following both laboratory and method-specific QA specifications.

Representativeness

Representativeness is defined as the degree to which data represent a characteristic of a population or set of samples and is a measurement of both analytical and field sampling precision. Representativeness is generally a function of the sampling design, including assessment of the entire study area and the distribution of historical results. Representativeness of a data set includes not only the comparability within a study, but comparisons to previous work and their ultimate indication of site condition. The project objective for representativeness is to provide data which is representative of the population of fish within the study reach. Representativeness has been addressed in part by the selection of multiple sampling stations. Because the current sampling design includes collection of composites of 5 resident fish species samples from multiple stations (in duplicate), variability as a result of potential undocumented sources or spurious "hot spots" is reduced both intra-site and across the study reach. The representativeness of the analytical data is further ensured through application of established procedures used in procuring and processing the samples. The representativeness goal will be satisfied by using experienced laboratory technicians to ensure that the samples are processed according to the methods, strictly following both laboratory and method-specific QA specifications. Representativeness can be documented by the relative percent difference between separately procured, but otherwise identical samples or sample aliquots. Tetra Tech will calculate and report precision estimates from replicate samples.

Completeness

Completeness is the comparison between the amounts of data that has been planned to be collected versus how much usable data was actually collected, expressed as a percentage. Data may be determined to be unusable in the validation process. The completeness objective for this project is 95%, expressed as the ratio of the valid data to the total data. Data will be considered valid if they are adequate for their intended use. Data validation is the process for reviewing data to determine its usability and completeness. If the completeness objective is not met, actions will be taken to improve performance. This may include an audit to evaluate the methodology and procedures, or may result in a recommendation to use a different method. Completeness is calculated as follows:

$$\%C = \frac{V}{T} \times 100$$

Where V = the number of valid measurements and T = the number of test measurement planned.

Comparability

Comparability is the degree to which data can be compared directly to previously collected data or the standard that the decision is made from. Comparability will be achieved for this project through consistent sampling locations, procedures, and analyses as outlined in this QAPP. Additionally, consideration is given to seasonal conditions and other environmental variations that could exist to

influence data results. Comparability is dependent on the proper design of the sampling program and will be satisfied by ensuring that the QAPP is followed and that proper sampling and analysis techniques are used. It is also dependent on recording field measurements using the correct units, where applicable.

The comparability objective is to provide analytical data for which the accuracy, precision, representativeness and reporting limit statistics are similar to these quality indicators generated by other laboratories for similar samples, and data generated by the laboratory over time. To meet the comparability goal, Tetra Tech and TestAmerica will use experienced laboratory technicians to ensure that the samples are processed according to the methods, strictly following both laboratory and method-specific QA specifications.

Sensitivity

The sensitivity objective is to ensure that laboratory measurements are useful in comparison to prevailing standards based on the media and target analytes of interest. For this study, Table 1 includes the laboratory reporting limit for all analytes of interest, while tables 2-4 include select standard criteria endpoints. While laboratory reporting limits are established in laboratory procedures based on predominant clients and client market requirements, concentration of calibration and spiking standards, and the ability to reliably generate quality data, sample concentrations observed between the laboratory reporting limits and laboratory-specific method detection limits will be reported as estimated values. Laboratory estimates will be reported with appropriate qualification in all data presentations.

A8. SPECIAL TRAINING REQUIREMENTS/CERTIFICATION

All members of the fish tissue sample processing and analysis team are required to have the education, knowledge, and experience needed to successfully perform all processing and analysis activities and related QA procedures. This includes knowledge and experience in the use of specialized equipment and instruments. The field and sample preparation/laboratory analysis QAPPs and SOPs will be distributed to all NNEPA, NNDFW, and Tetra Tech personnel that will participate in the study. Materials will include detailed instructions for each laboratory procedure. All personnel will be required to read the SOPs and QAPPs, and verify that they read the materials and understood the procedures and requirements.

The fish tissue samples will be prepared at the Tetra Tech Biological Research Facility in Baltimore, Maryland. All laboratory staff involved in the preparation of fish tissue samples are experienced with standard processing procedures, the use of associated equipment, and standard QA/QC procedures. All staff participating in work for this project will be proficient in the procedures as detailed in Appendix A, Standard Operating Procedures for the San Juan River Fish Tissue Study Tissue Preparation, Homogenization, and Distribution.

All laboratory staff involved in fish tissue sample analyses will be proficient in the required procedures for each analytical method (i.e., EPA Methods 6020A and 7471B, provided in Appendix B). All laboratory staff will be proficient in the tasks required by TestAmerica's existing quality system, as described in TestAmerica's QA Manual (TestAmerica 2015). All staff involved in analytical data review and assessment will be proficient in data review, and no specialized training is required for data reviewers for this project.

A9. DOCUMENTS AND RECORDS

All tissue sample preparation tasks will be thoroughly documented according to the Tetra Tech fish tissue sample preparation SOPs (Appendix A). All analytical tasks will be thoroughly documented according to EPA's analytical methods (Appendix B) and TestAmerica's QA Manual (TestAmerica 2015). The major deliverables requirements for the sample preparation laboratory are summarized below:

- The sample preparation laboratory must prepare and submit a weekly progress report to the NNEPA PM to document the status of fish sample preparation activities and provide information specified in the SOW.
- The analytical laboratory must report the results of the equipment rinsate analysis results associated with that sample batch.

The major deliverables requirements for the analytical laboratory are summarized below:

- The analytical laboratory must provide reports of all results required from analyses of samples.
- Summary level data will be submitted in electronic format and will include the following information: site number, sample number, analyte name and CAS number, laboratory sample ID, measured amount, reporting units, sample preparation date, and analytical batch ID (if applicable).

All project documents and records will be maintained by the NNEPA and Tetra Tech during the project, and retained for a period of two years following completion of the project (unless otherwise directed by the NNEPA).

Group B: Data Generation and Acquisition Elements

B1. SAMPLING PROCESS DESIGN (EXPERIMENTAL DESIGN)

The objective of the San Juan River Fish Tissue Study is to provide a screening level assessment to help identify the prevailing human health risk associated with fish consumption subsequent to the GKM spill, and will be based on monitoring current contaminant levels in fish (specifically metals). The sampling design is detailed in the *Quality Assurance Project Plan Sample Collection Activities for the San Juan River Fish Tissue Contaminant Study* (Volume 1 of 2) (Tetra Tech 2017), and is summarized below.

A total of five locations on the San Juan River between Farmington, New Mexico and Bluff, Utah will be sampled. The sites were selected based on NNEPA, NNDFW, and USFWS expertise and recommendations to best represent areas of the San Juan River that are commonly fished. The Field Team will collect a composite sample of five individuals of the same species from each sampling location. The field sampling period is April 2017. The target population for the San Juan River Fish Tissue Study is the population of fish residing or moving through the San Juan River between Farmington, New Mexico and Bluff, Utah, that are commonly consumed by humans.

B2. SAMPLING METHODS

Sampling methods are detailed in the *Quality Assurance Project Plan Sample Collection Activities for the San Juan River Fish Tissue Contaminant Study* (Volume 1 of 2) (Tetra Tech 2017). These sampling methods are summarized below.

The Field Team will be equipped with valid Scientific Collection Permits for the San Juan River study reach and an array of active gear appropriate for the location, sampling conditions, and targeted species. As fish specimens are obtained, they will immediately be identified to species by the team's fisheries biologist. Non-target species will be returned to the river. Each specimen of the selected target species will be measured to determine total body length in millimeters. When five individuals of the target species meeting the size criteria have been identified, the species name, specimen lengths, and all other site and sampling information will be recorded on the Field Record Form. The primary target species for the San Juan River Fish Tissue Study is Channel Catfish (*Ictalurus punctatus*), a species commonly consumed by humans and one that may potentially accumulate high concentrations of contaminants (i.e., a bottom-dwelling species with potential close contact with river bottom sediments). Every effort will be made to collect the target species and number of fish; however, the outcome of field sampling efforts will ultimately depend on the natural diversity and abundance of fish at the sampling sites.

B3. SAMPLE HANDLING AND CUSTODY

Whole fish samples will be shipped frozen on dry ice, and will be inspected promptly on receipt. As samples arrive, the sample custodian at the sample preparation laboratory:

- Checks that each shipping container has arrived undamaged and verifies that samples are still frozen and in good condition.
- Checks the temperature of one of the samples in the cooler using a thermometer that reads to at least -20 degrees Celsius (°C), or an infra-red (IR) temperature "gun" and records the reading on the sample tracking form.
- Verifies that all associated paperwork is complete, legible, and accurate.
- Compares the information on the label on each individual fish specimen to the chain of custody form for each composite and verifies that each specimen was included in the shipment and is properly wrapped and labeled.
- Transfers the samples to the freezer for storage.

The sample preparation laboratory notifies the NNEPA PM immediately about any problems encountered upon receipt of samples. Problems involving sample integrity, conformity, or inconsistencies for fish tissue samples are required to be reported in writing (e.g., by email) as soon as possible following sample receipt and inspection. Following sample processing, the sample preparation laboratory must store sample aliquots frozen to less than or equal -20°C until they are shipped to the analytical laboratory. Frozen whole body tissue samples generally have a holding time of one year.

Frozen sample aliquots will be shipped frozen on dry ice, and will be inspected promptly on receipt. As samples arrive, the designated sample receiving custodian at the analytical laboratory:

- Checks that each shipping container has arrived undamaged and verifies that samples are still frozen and in good condition.
- Checks the temperature of one of the samples in the cooler using a thermometer that reads to at least -20 degrees Celsius (°C), or an infra-red (IR) temperature "gun" and records the reading on the sample tracking form.
- Verifies that all associated paperwork is complete, legible, and accurate.
- Compares the information on the label on each aliquot jar to the chain of custody form, and verifies that each jar is intact and properly wrapped and labeled.
- Assigns each sample container a unique sample identification number that is cross-referenced to the client identification number such that traceability of test samples is unambiguous and documented. Each sample container is affixed with a durable sample identification label.
- Ensures accurate login of samples into the Laboratory Information Management System (LIMS).
- Transfers the samples to the freezer for storage.

The Tetra Tech PM notifies the NNEPA PM immediately about any problems encountered upon receipt of samples. Problems involving sample integrity, conformity, or inconsistencies are required to be reported in writing (e.g., by email) as soon as possible following sample receipt and inspection.

B4. PREPARATION AND ANALYTICAL METHODS

Fish Tissue Sample Preparation

The Tetra Tech Biological Research Facility in Baltimore, Maryland will serve as the fish sample preparation laboratory (prep lab). In this role, Tetra Tech is responsible for filleting each valid fish sample, homogenizing the fillet tissue, preparing the required number of fish tissue aliquots for analysis and archive, shipping the fish tissue aliquots for each analysis to the analytical laboratory, and storing archived fish tissue samples in a freezer at their facility. The specific procedures for fillet tissue sample preparation activities are described in Appendix A.

Before sample preparation, trained lab technicians will complete a relative fish length comparison to confirm that field crews attached the correct label to each fish in the composite sample. Each fish is then weighed to the nearest gram, rinsed with deionized water, placed on a clean glass cutting board, and scaled. The filleting process involves removing the fillet (with skin on and belly flap [ventral muscle] attached) from both sides of each fish. Fillets are composited using the "batch" method (all of the fillets from the individual specimens that make up the sample are homogenized together, regardless of each specimen's proportion to one another) as opposed to the "individual" method (equal weights of tissue from each specimen are added together).

An electric meat grinder is used to prepare homogenate samples. Entire fillets (with skin and belly flap) from both sides of each fish are homogenized, and the entire homogenized volume of all fillets from the fish sample is used to prepare the tissue sample. Tissues are mixed thoroughly until they are completely homogenized as evidenced by a fillet homogenate that consists of a fine paste of uniform color and texture. The collective weight of the homogenized tissue from each sample is recorded to the nearest gram (wet weight) after processing. Tetra Tech will prepare fillet tissue samples and sample aliquots according to the specifications listed in the fish sample preparation procedures in Appendix A.

Analysis of Metals

Fish tissue samples will be analyzed by TestAmerica using Method 6020A for a suite of 24 metals and Method 7471B for mercury. Aqueous equipment rinsate samples (Appendix A) will be analyzed by TestAmerica using these same two methods. The full methods with method-specific QA procedures are presented in Appendix B.

Method 6020A (*Inductively Coupled Plasma-Mass Spectrometry, Revision 1*) is an EPA method with instrument detection limits generally below 0.1 µg/L. Less sensitive elements (e.g., Se and As) and desensitized major elements may be 1.0 µg/L or higher. Tissue sample results are reported based on the wet weight of the tissue sample, in milligrams per kilogram (mg/Kg). The method measures ions produced by a radio-frequency inductively coupled plasma (EPA 1998). Method reporting limits for this project are provided in Table 1 of this QAPP.

Method 7471B (*Mercury in Solid or Semisolid Waster [Manual Cold-Vapor Technique], Revision 2*) is an EPA method with a typical instrument detection limit of 0.0002 mg/L. Tissue sample results are reported based on the wet weight of the tissue sample, in milligrams per kilogram (mg/Kg). This method uses cold-vapor atomic absorption and is based on the absorption of radiation by mercury vapor (EPA 2007). Method reporting limits for mercury for this project are provided in Table 1 of this QAPP.

During the course of the homogenization of the fish tissue samples, equipment rinsate samples (Appendix A) will be analyzed by TestAmerica. TestAmerica is analyzing these aqueous samples using Method 6020A and Method 7471B. Rinsate results are reported based on the volume of the rinsate sample, in micrograms per liter (µg/L).

B5. QUALITY CONTROL

The quality of data generated for this project is ensured through the use of trained, experienced personnel that will consistently follow the SOPs (Appendix A), method, and project protocols. Project staff will document all project activities according to the SOPs. The field and sample preparation/analytical QAPPs and SOPs will be distributed to the appropriate project staff, who will verify in writing that they have read the materials and understand the procedures and requirements. If there is any indication that sample integrity or data quality requirements have not been met, the Tetra Tech QA Officer will be notified immediately (with an accompanying explanation of the problems encountered).

Two (replicate) composite samples will be collected at each of the 5 sampling sites, one "standard" sample and one "duplicate" sample. Each sample will be analyzed independently. The replicate composites at each site will be of the same species, number of specimens, and size range. Replicate analysis will be used to assess consistency and representativeness of the samples, as well as providing a basis for an estimate of variance. (*Note: "field blanks" are sometimes collected as negative controls for certain types of samples. However, they are not typically collected for the sampling of fish tissue, and will not be collected for this study).*

Laboratory QC is addressed through implementation of established, documented methods and SOPs. Routine laboratory QC include instrument calibration and calibration verification, and preparation and analysis of negative (rinsate [homogenization], instrument, calibration, and digestion blanks) and positive

controls (LCS or standard reference materials), spiked samples (MS), and sample duplicates (lab duplicates) or spiked sample duplicates (MSDs). Further discussion of project QC requirements, implementation, and common corrective actions follows.

Fish Tissue Sample Preparation

The project-specific QC procedures for fish sample preparation include preparation and testing of equipment rinsate samples and homogeneity testing, using lipids as a surrogate. During sample preparation, Tetra Tech will prepare one set of rinsate samples as described in Appendix A. The rinsate results will be reviewed by Tetra Tech to check the effectiveness of decontamination procedures and reported to NNEPA. The sample preparation laboratory may continue to process samples during that review process. If results are deemed unsatisfactory, the sample preparation laboratory may not continue processing until the issue has been identified and corrective actions are taken.

Analysis of Metals

TestAmerica will use methods 6020A and 7471B to meet the study requirements. These analytical methods are currently accepted and approved by the EPA. TestAmerica maintains SOPs for the operation of analytical equipment as well as for the handling of samples. All instructions, reference methods and manuals relevant to the working of the laboratory are readily available to all staff. General quality control samples and activities for TestAmerica are summarized in Table 6 below. TestAmerica will adhere to all method-specific QA procedures, which are included in the full methods presented in Appendix B.

Table 5: General Acceptance Criteria and Corrective Action Procedures for TestAmerica

QC Activity	Acceptance Criteria	Corrective Action
Initial Instrument Blank	- Instrument response < MDL.	- Prepare another blank. - If same response, determine cause of contamination: reagents, environment, instrument equipment failure, etc.
Initial Calibration Standards	- Correlation coefficient >0.99 or standard conc. value. - % Recovery within acceptance range. - See details in Method SOP.	- Reanalyze standards. - If still unacceptable, remake standards and recalibrate instrument.
Independent Calibration Verification	- % Recovery within control limits.	- Remake and reanalyze standard. - If still unacceptable, then remake calibration standards or use new primary standards and recalibrate instrument.
Continuing Calibration Standards	% Recovery within control limits.	- Reanalyze standard. - If still unacceptable, then recalibrate and rerun affected samples.
Matrix Spike / Matrix Spike Duplicate (MS/MSD)	- % Recovery within limits documented in LIMS.	- If the acceptance criteria for duplicates or matrix spikes are not met because of matrix interferences, the acceptance of the analytical batch is determined by the validity of the LCS. - If the LCS is within acceptable limits the batch is acceptable. - The results of the duplicates, matrix spikes and the LCS are reported with the data set. - For matrix spike or duplicate results outside criteria the data for that sample shall be reported with qualifiers.

QC Activity	Acceptance Criteria	Corrective Action
Laboratory Control Sample (LCS)	- % Recovery within limits specified in LIMS,	- Batch must be re-prepared and re-analyzed. 1) when the acceptance criteria for the positive control are exceeded high and there are associated samples that are non-detects, then those non-detects may be reported with data qualifying codes; 2) when the acceptance criteria for the positive control are exceeded low generally with low bias samples are re-prepared and reanalyzed.
Surrogates	- % Recovery within limits of method or within 3 standard deviations of the historical mean.	- Individual sample must be repeated. Place comment in LIMS. - Surrogate results outside criteria shall be reported with qualifiers.
Method Blank (MB)	< Reporting Limit; For common lab contaminants, no analytes detected at greater than and equal to RL.	- Reanalyze blank. - If still positive, determine source of contamination. If necessary, reprocess entire sample batch. Report blank results. - Qualify the result(s) if the concentration of a targeted analyte in the MB is at or above the reporting limit and is > 1/10 of the amount measured in the sample.
Internal / External Audits	- Defined in Quality documentation (SOPs, QAPP, etc.)	- Non-conformances must be investigated through CAR system and necessary corrections must be made.

B6. INSTRUMENT/EQUIPMENT TESTING, INSPECTION, AND MAINTENANCE

There are no analytical instruments used in the preparation of the fillet tissue samples. However, the balances used to weigh the whole fish and the tissue sample aliquots are inspected and serviced on a regular schedule and the homogenization equipment (meat grinder) will be inspected when it is reassembled after cleaning between samples. Balances are also subject to daily use verification using in-house NIST weights encompassing the working range for use.

All analytical instrumentation associated with the rinsate analyses and tissue sample analyses will be inspected and maintained as described in the respective analysis methods and laboratory methods (Appendix B). Calibration is verified routinely in the laboratory, and this verification is considered part of testing and inspection, as well as calibration.

B7. INSTRUMENT/EQUIPMENT CALIBRATION AND FREQUENCY

All equipment will be maintained as per manufacturer's recommendations and instructions. The balances used to weigh the whole fish and the sample aliquots are calibrated on a regular basis. Calibrations will be verified at the beginning of each day that the balances are used.

Calibration of analytical instrumentation is essential to the production of quality data. Strict calibration procedures will be followed for each method. These procedures determine and document the method reporting limits, the working range of the analytical instrumentation, and any daily fluctuations that may occur. Sufficient raw data records will be retained at the laboratory to allow an outside party to

reconstruct all facets of the initial calibration. Records will contain the following: calibration date, method, instrument, analyst(s) initials or signatures, analysis date, analytes, concentration, response, type of calibration (Avg RF, curve, or other calculations that may be used to reduce instrument responses to concentration.) If the initial calibration results are outside of the acceptance criteria, corrective action will be performed and any affected samples will be reanalyzed if possible. If the reanalysis is not possible, any data associated with an unacceptable initial calibration will be reported with appropriate data qualifiers. Detailed calibration SOPs are included in the TestAmerica Quality Assurance Manual (TestAmerica 2015).

B8. INSPECTION/ACCEPTANCE OF SUPPLIES AND CONSUMABLES

The inspection and acceptance of laboratory supplies and consumables associated with fish tissue sample analyses are addressed in the existing overall quality systems for TestAmerica. There are no additional requirements specific to this project. Please refer to the TestAmerica Quality Assurance Manual (TestAmerica 2015).

B9. NONDIRECT MEASUREMENTS

Non-direct measurements are not required for this project.

B10. DATA MANAGEMENT

Data management procedures for the San Juan River Fish Tissue Study are based on similar studies conducted by Tetra Tech. These procedures ensure the effective, efficient documentation of sample tracking, data tracking, data inspection, data quality assessment, and database development. All staff involved with fish tissue sample preparation and analysis activities will follow the procedures summarized below.

Tetra Tech (the sample preparation laboratory) and TestAmerica (the analytical laboratory) will use standardized data templates to record all data associated with the study (see Appendix B). Both labs will maintain all records and documentation associated with the preparation of samples and the rinsates and the analyses of the fish tissue samples and associated QC results for five years upon completion of the study. All data deliverables and documentation will be sequentially paginated and clearly labeled with the laboratory name, and associated sample numbers.

Any electronic deliverables will be similarly labeled. Electronic data will be prepared for all sample and QC analyses for the project, and submitted in a format selected by the PM from the laboratory's available file specification. An example of an electronic data deliverable (EDD) file specification is presented in Table 6.

Tetra Tech and TestAmerica will follow comprehensive data management procedures that are consistent with those presented in Good Automated Laboratory Practices, EPA Office of Administration and Resources Management (USEPA 1995) and with data management procedures approved by the National Environmental Laboratory Accreditation Conference (NELAC). Tetra Tech and TestAmerica's data management plans are incorporated in their overall quality management plans.

Table 6. Example EDD Specification

Data Field	Data Field Summary
PROJECT	Key used to identify the project associated with the sampling event
SITE	ID for the site at which the sample was collected at
SDG_WONO	Laboratory Sample Delivery Group (SDG).
FIELDSAMPLEID	Primary key used to identify each distinct sample collected in the field, for a specific sampling day or episode.
LABSAMPLEID	Laboratory assigned sample identification.
MATRIX	Matrix represented by the sample that was originally collected.
METHOD	Analysis method as specified on the Chain-of-Custody
SAMPLEDATE	Date the sample was collected on
EXTRACT_PREPDATE	Date the sample was extracted on
ANALYSISDATE	Date that the sample began to be analyzed at the laboratory
PERCENTSOLIDS	Percent solid of the sample portion used in this analysis.
CAS_ID	Chemical Abstract Service (CAS) number for which results are being reported.
ANALYTE	Analyte or compound name for which results are being reported.
RESULT	Result, concentration, or reporting limit of the analyte, parameter or compound (in a text data format).
UNITS	Unit of measure (e.g. UG/L) for which results are being reported.
DILUTION_FACTOR	Dilution Factor
DETECT_LIMIT	Detection Limit
DLQUALIFIER	Dilution Qualifier
LABQUALIFIER	Laboratory Qualifier
COMMENTS	Comments

Group C: Assessment and Oversight Elements

C1. ASSESSMENT AND RESPONSE ACTIONS

Assessment and response actions ensure that sample collection activities are conducted according to the SOPs, and that the project MQOs and DQOs are met. The project QA program includes performance and system audits with independent checks of the analytical data. Either type of audit could indicate the need for corrective action. The essential steps in the QA program are:

* identify the problem,
* investigate and determine the cause of the problem,
* implement appropriate corrective action,
* verify that the corrective action has eliminated the problem, and
* proceed with work.

Tetra Tech and TestAmerica each have a comprehensive QA program; when performing work for this study, each laboratory will follow those requirements. The following sections describe general assessment and response actions in place to ensure that sample preparation and analytical activities are conducted as prescribed and that the performance criteria defined for the study are met.

Performance audits

Performance audits are qualitative checks on project activities. TestAmerica participates semi-annually in performance audits conducted through the analysis of PT samples provided by a third party. Project specific performance audits will not be conducted.

Quality Systems Audit

A quality system audit (QSA) is used to verify, by examination and evaluations of objective evidence, that applicable elements of the quality system are appropriate and have been developed, documented, and effectively implemented in accordance and in conjunction with specified requirements. The focus of these assessments is on the quality system processes – not on evaluating the quality of specific products or judging the quality of environmental data or the performance of personnel or programs. Both Tetra Tech and TestAmerica require and conduct an annual quality systems audit to ensure compliance with analytical methods and SOPs, Data Integrity and Ethics Policies, quality systems, data review, quality controls, preventive action and corrective action.

Technical Audit

The laboratory contracts require that the laboratories be prepared for and willing to undergo an on-site, or technical systems, audit of its facilities, equipment, staff, sample processing and rinsate analysis, tissue analysis, training, record keeping, data validation, data management, and data reporting procedures. An audit will be conducted only if the results of the readiness reviews, data quality audits, and surveillance suggest serious problems that warrant on-site examinations and discussion with laboratory personnel. If such an audit is determined to be necessary, a standardized audit checklist will be used to facilitate an audit walkthrough and document audit findings. Audit participants may include the NNEPA Project Manager and/or the Tetra Tech QA Officer.

Surveillance

The Tetra Tech Laboratory Coordinator will track all work performed by the sample preparation laboratory and the analytical laboratory. This coordination will be with staff at both labs regarding fish tissue sample shipments, the receipt and condition of the samples on arrival and the progress of the analyses. When the samples are shipped from the field to the sample preparation laboratory, the Laboratory Coordinator will immediately begin tracking the shipment until arrival the following morning. She will verify that the samples arrived in good condition, and if a problem is noted, will work with the laboratory and NNEPA to resolve it as quickly as possible to ensure data integrity.

The Tetra Tech Laboratory Coordinator will communicate with laboratory staff regularly to monitor the progress of sample preparation and analyses of the tissue samples. If technical problems are encountered during sample preparation, tissue analyses, or rinsate analysis she will identify the appropriate technical expert within Tetra Tech and/or TestAmerica to assist in resolving the problem, and work with NNEPA to identify and implement a solution to the problem.

Product Review

The Tetra Tech PM will review the sample preparation records and the metals analyses results. The results of those reviews will be documented in emails to the NNEPA PM. All electronic data deliverables will be reviewed by the Tetra Tech PM before submittal to the NNEPA PM.

C2. REPORTS TO MANAGEMENT

The Tetra Tech Laboratory Coordinator will provide the NNEPA PM with a weekly status report that describes all of the fish samples prepared and/or analyzed during the previous week. The Tetra Tech Laboratory Coordinator will track the receipt of data submissions for tissue analyses and advise the NNEPA PM of progress on a monthly basis.

Group D: Data Validation and Usability Elements

D1. DATA REVIEW, VERIFICATION, AND VALIDATION

Tetra Tech will be responsible for reviewing data entries and transmittals for errors, completeness, and adherence to project QA requirements. All laboratory results and calculations will be reviewed by the Laboratory Manager prior to data submission to Tetra Tech. Any errors identified during this review will be returned to the analyst for correction prior to submission of the data deliverable. The Laboratory Manager will verify that the final package is complete and compliant with the contract, and will sign each data submission to certify that the package was reviewed and determined to be in compliance with the terms and conditions of the contract.

Data verification ensures that project staff know what data were produced, if they are complete, if they are contractually compliant, and if they meet the objectives of the study. Data validation is the process of evaluating the quality of the results relative to their intended use. The validation process is designed to identify data quality issues uncovered during the verification process that may affect the intended use.

The Tetra Tech PM will conduct reviews of the QC sample results for the rinsates of the sample processing equipment. He will determine if they meet the project objectives in this QAPP, and report the findings to the NNEPA PM. The Tetra Tech PM will review the data for metal analyses and determine if they meet the project objectives in this QAPP.

D2. VERIFICATION AND VALIDATION METHODS

The Tetra Tech QA Officer will check each laboratory deliverable for completeness. All data elements in each laboratory deliverable will be evaluated to verify that results for all specified samples are provided, that data are reported in the correct format, and that all relevant information, such as preparation and analysis logs, are included in the data package. The Tetra Tech QA Officer will then verify that the laboratory correctly performed the required analytical procedures and was able to demonstrate a high level of precision and accuracy. She will evaluate laboratory QC elements including the laboratory control samples, method blanks, and matrix spike samples.

The Tetra Tech QA Officer will attempt to reconcile any discrepancies or deficiencies in the records with the associated lab personnel, and they will be reported to the Tetra Tech PM and NNEPA PM. The Tetra Tech QA Officer will initiate corrective action procedures immediately if needed.

The Tetra Tech QA Officer will perform a data quality and usability assessment to evaluate the quality of project data against the performance criteria. Overall quality of a particular data set will be evaluated, rather than individual QC failures. The results of this assessment will be documented in a report and submitted to the NNEPA PM.

D3. RECONCILIATION WITH USER REQUIREMENTS

The QC results for the rinsate analysis will be assessed against the QC acceptance criteria. Although the sample preparation laboratory will be permitted to work before these results are available, Tetra Tech will track laboratory performance, notify the NNEPA PM of any issues, initiate corrective actions, and track progress by the sample preparation laboratory.

The QC results for the analyses of the fish tissue samples for the suite of metals will be assessed against the QC acceptance criteria for the analyses. Tetra Tech will track laboratory performance, notify the NNEPA PM of any issues, initiate corrective actions, and track progress of the analytical laboratory.

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Appendix A

Standard Operating Procedures

Fish Tissue Sample Preparation Procedures for the San Juan River Fish Tissue Study

Standard Operating Procedures

Fish Tissue Sample Preparation Procedures for the San Juan River Fish Tissue Study

Scope and Applicability: This Standard Operating Procedure (SOP) describes the procedures that the sample preparation laboratory will follow when preparing fish tissue samples for the NNEPA San Juan River Fish Tissue Study. Adherence to these procedures will ensure that fish tissue preparation activities are performed consistently across all study samples.

Fish tissue sample preparation procedures are presented below as sequential steps, and include specific equipment, materials, and methods required to perform these activities only.

Responsibility and Personnel Qualifications: These procedures will be used by the fish tissue sample preparation laboratory that has been authorized by the Tetra Tech PM.

Composite Sample Classifications

Routine sample – A routine composite sample consists of five individual adult fish of a single species that meet length requirements (i.e., length of the smallest specimen in the composite is at least 75% of the length of the largest individual). Fillets from both sides of all five fish will be removed (total of 10 fillets) and homogenized to prepare one composite fillet sample.

Non-routine sample – A non-routine sample is any sample that does not meet the definition of a routine sample, including those that do not meet the 75% rule and those with fewer or greater than five fish. If non-routine samples are sent to the sample preparation laboratory, the Tetra Tech PM and the NNEPA PM will consider the sample, determine if it is useable, and provide instructions for processing the non-routine samples. These instructions may include discarding some of the fish in the composite sample based on size before proceeding with filleting and homogenizing. In cases when fewer or more than five fish were collected, instructions may include processing some or all of those fish in the composite sample.

Each of the five fish in the routine samples must be filleted before homogenization. For non-routine composites, only the designated specimens (identified by specimen number) will be filleted and homogenized. For both types of samples, the specimens to be included in each composite must be scaled (i.e., scales removed) and both fillets from each specimen prepared as skin-on fillets (belly-flap included) to form the fillet composites. Depending on the species retained and NNEPA/NNDFW knowledge of local consumption practices, skin may be removed before homogenization (e.g., for catfish species).

Sample Receipt and Storage

Fish samples for the San Juan River Fish Tissue Study will be collected within the first two weeks of April, 2017. Samples will be shipped directly from the field sampling crew to the sample preparation laboratory for storage and processing. The sample preparation laboratory must have sufficient freezer space to store up to 10 unprocessed fish composite samples (e.g., 10 5-fish composites) at a temperature of less than or equal to -20°C from the time of receipt until completion of sample processing, and sufficient freezer space to store homogenized tissue aliquots from these samples prior to distribution to the analytical laboratory.

1. Although samples will be shipped frozen on dry ice, they must be inspected promptly upon receipt. As samples are received, the sample custodian must:
   a) Check that each shipping container has arrived undamaged and verify that samples are still frozen and in good condition.
   b) Check and record the temperature of one of the samples in the cooler using a thermometer that reads to at least -20°C, or an infra-red (IR) temperature gun.
   c) Verify that all associated paperwork is complete, legible, and accurate.
   d) Compare the information on the label on each individual fish specimen to the sample tracking form for each composite and verify that each specimen was included in the shipment and is properly wrapped and labeled.
   e) Notify the Tetra Tech PM that samples were received and of any discrepancies in the paperwork identified above.
   f) Transfer the samples to the freezer for storage.
2. Notify the Tetra Tech PM immediately about any problems upon receipt of samples. Problems involving sample integrity, conformity, or inconsistencies for fish tissue samples must be reported to the NNEPA PM in writing (e.g., by email) as soon as possible following sample receipt and inspection.

Following sample processing, the sample preparation laboratory must store sample aliquots frozen to less than or equal -20°C until they are distributed to the analytical laboratory.

Sample Handling

The whole fish must remain frozen at less than or equal to -20°C until the sample processing laboratory receives composite-specific processing instructions from the Tetra Tech PM. Samples to be processed must be retrieved from the freezer, with their associated paperwork, and allowed to partially thaw before they can be processed.

3. The Tetra Tech PM will provide sample processing instructions to the laboratory personnel. The instructions consist of an Excel spreadsheet that details the site and sample identifiers. The spreadsheet will list the following fields for each individual fish specimen in a given composite sample:
   a. Site ID
   b. Date of collection

c. Sample ID, that is a four character code with site number (one-digit, i.e., 1-5), composite ID (one-digit, i.e., A or B to differentiate the 2 composites collected at each site), and specimen number (two-digits, i.e., 01-05).
d. Common name for the fish species
e. Measured length of each specimen in mm
f. Composite classification (Routine, Non-Routine, or Invalid)
g. Deviation (e.g., why it is not routine or not valid)
h. Instructions (sample-specific details about which fish to process).

When retrieving samples from the freezer, the sample custodian must verify that all associated paperwork stored with the samples is complete, legible, and accurate. The custodian will compare the information on the label on each individual fish specimen to the processing instructions and notify the Tetra Tech PM of any discrepancies between the sample labels and the Excel spreadsheet. Problems involving sample paperwork, sample integrity, or custody inconsistencies for all fish tissue samples must be reported to the Tetra Tech PM in writing (e.g., by email) as soon as possible following sample retrieval and inspection. Do not proceed with sample processing until discrepancies are resolved.

Filleting and Homogenization Procedures

4. Prior to preparing any samples, thoroughly clean utensils and cutting boards using the following procedures:
    a. Wash with a detergent solution (phosphate- and scent-free) and warm tap water
    b. Rinse three times with warm tap water
    c. Rinse three times with DI water
    d. Rinse with acetone
    e. Rinse three times with DI water
    f. Rinse with (not soak in) 5% nitric acid
    g. Rinse three times with DI water

To control contamination, separate sets of utensils and cutting boards must be used for scaling fish (if necessary) and for filleting fish.

5. Put on powder-free nitrile gloves before unpacking individual fish specimens. As samples are unpacked and unwrapped, inspect each fish carefully to verify that it has not been damaged during collection or shipment. If damage (e.g., tearing the skin or puncturing the gut) is observed, document it in the laboratory project log sheet and notify the Tetra Tech PM before proceeding further.
6. Begin processing the specimens by laying them out in order by specimen number and allow them to partially thaw to the point that each specimen can be laid relatively flat. Using the length data on the specimen label, confirm that the specimen ID for the longest specimen recorded on the tracking form is the same as the specimen ID on the label of the longest specimen. Repeat this relative length comparison for each of the other specimen IDs to ensure that the length orders based on the recorded lengths on the field form are consistent with the specimen IDs on the

individual fish labels. If discrepancies are observed, document them in the laboratory project log and notify the Tetra Tech PM before proceeding further.

7. Weigh each fish to the nearest gram (wet weight) prior to any sample processing. Enter weight information for each individual fish into a laboratory project log. Individual specimen weights eventually will be transferred to spreadsheets for submission to the Tetra Tech PM.
8. Rinse each fish with deionized water to remove any detritus that may be on specimens from sample handling in the field. Use HDPE wash bottles for rinsing fish and for cleaning homogenization equipment and utensils.
9. Before beginning the scaling process for the first fish in the composite, put on new powder-free nitrile gloves. (Gloves must be changed between composites, but the same gloves may be used for all fish within a given composite.) Fish with scales must be scaled (and any adhering slime should be removed) prior to filleting. Scale the fish by laying it flat on a clean glass cutting board and scraping from the tail to the head using a stainless steel scaler or the blade-edge of a clean stainless steel knife. Filleting can proceed after all scales have been removed from the skin and a separate clean cutting board and fillet knife are prepared or available.
10. Place each fish on a clean glass cutting board in preparation for the filleting process. Note that filleting should be conducted under the supervision of an experienced fisheries biologist, if possible. Ideally, fish should be filleted while ice crystals are still present in the muscle tissue. Fish should be thawed only to the point where it becomes possible to make an incision into the flesh. Remove both fillets (lateral muscle tissue with skin attached) from each fish specimen using clean, high-quality stainless steel knives. Include the belly flap (ventral muscle and skin) with each fillet. Care must be taken to avoid contaminating fillet tissues with material released from inadvertent puncture of internal organs. In the event that an internal organ is punctured, rinse the fillet with deionized water immediately after filleting and make a note on the laboratory project log sheet that a puncture has occurred. Bones still present in the tissue after filleting should be carefully removed using the tip of the fillet knife or a clean pair of forceps. Depending on the species retained and NNEPA/NNDFW knowledge of local consumption practices, skin may be removed before homogenization (e.g., for catfish species). Remove the skin from each fillet using the stainless steel fillet knife.
11. Samples should be homogenized partially frozen for ease of grinding. Composite the fillets using the "batch" method, in which all of the fillets from the individual specimens that comprise the sample are homogenized together, regardless of each individual specimen's proportion to one another (as opposed to the "individual" method, in which equal weights of tissue from each specimen are added together).
12. Process each sample using a size-appropriate homogenization apparatus (e.g., automatic grinder or high-speed blender). Entire fillets (with belly flap) from both sides of each fish must be homogenized, and the entire homogenized volume of all fish fillets from the composite will be used to prepare the composite. Mix the tissues thoroughly until they are completely homogenized as evidenced by a final composite sample that consists of a fine paste of uniform color and texture. Grinding of tissue may be easier when tissues are partially frozen. Chilling the grinder briefly with a few small pieces or pellets of dry ice may also keep the tissue from sticking to the equipment. Pellets of dry ice also may be added to the tissue as it enters the grinder.

13. Grind the sample a second time, using the same grinding equipment. This second grinding should proceed more quickly. The grinding equipment does not need to be cleaned between the first and second grinding of the sample. The final sample must consist of a fine paste of uniform color and texture. If there are obvious differences in color or texture, grind the entire sample a third time.
14. Measure the collective weight of the homogenized fillet tissue from each composite to the nearest gram (wet weight) after processing and record the total homogenized tissue weight of each composite on a laboratory project log sheet. The collective weight of the homogenized tissue from each sample will be transferred to spreadsheets for submission to the Tetra Tech PM. At least 20 g of homogenized tissue will be needed to fill the containers in Table 1 with their minimum acceptable masses. If a sample does not yield at least 20 g of homogenized tissue, contact the Tetra Tech PM via email immediately and await instructions. As appropriate, place any less-than-20-g homogenized samples in the freezer while waiting for instructions.
15. After the final (second or third) grinding, clean the grinding equipment and all other sample preparation equipment using the procedures described in Step 19.

Aliquoting and Distribution Procedures

16. The sample preparation laboratory will prepare one bulk homogenate tissue aliquot per fish composite sample and use it to fill the pre-cleaned sample containers specified for each type of sample listed in Table 1, following the procedures described in Step 17. All containers will be provided by the analytical laboratory. Documentation of their cleanliness provided by the vendor must be retained by the sample preparation laboratory and provided to the Tetra Tech PM. The target masses listed in Table 1 are designed to provide enough tissue for multiple analyses of each sample and analyte type, including tissue for QC purposes, as needed. The sample preparation laboratory should not exceed those target masses when filling the containers.

Table 1. San Juan River Fish Tissue Study Tissue Sample Aliquots

Analyte	Method	Target Mass	Container Type
Suite of 24 Metals	Tissue 6020A	5 g	Clear glass, 125 mL, wide mouth
Mercury (CVAA)	Tissue 7471B	5 g	Clear glass, 125 mL, wide mouth
Moisture Content	Tissue 2540G	10 g	Clear glass, 125 mL, wide mouth
Bulk Archive	Archive	250 g	Clear glass, 500 mL, wide mouth
Small Archive	Archive	50 g	Clear glass, 125 mL, wide mouth

* *In the event of insufficient fish tissue mass to prepare the required number of aliquots, contact the Tetra Tech PM for instructions.*

17. Prepare the sample aliquots for the suite of 24 metals, mercury, and moisture content. Weigh an appropriate clean sample container (Table 1) to the nearest 0.5 g and record the weight. Transfer sufficient aliquots of ground sample to the container to achieve the target mass for that container in Table 1, weigh the container again, record the weight, and determine the weight of the aliquot to the nearest 0.5 g by difference.

When filling jars, leave sufficient space at the top of each jar to allow for expansion of the tissue as it freezes. In no case should jars be filled beyond 80% capacity, as this may result in breakage on freezing. Wipe off the outside of the jars to remove any tissue residue or moisture. Fill out a label for each container using a waterproof marker. Include the following information (at a minimum) on each label:

- site identification number,
- sample identification number,
- analysis type (e.g., mercury),
- aliquot weight (to the nearest 0. and5 gram),
- preparation date (e.g., mm/dd/yyyy).

Affix the label to the container with clear wide tape. Place each container inside one heavy-weight food-grade self-sealing plastic freezer bag to avoid sample loss due to breakage. Freeze the tissue aliquots at -20°C, and maintain samples in the freezer until directed by the Tetra Tech PM to ship them to the analytical laboratory.

18. The archive sample jars are not filled until after sufficient volume for the suite of 24 metals, mercury, and moisture content samples have been collected. The remaining tissue mass is used to create archive samples. Begin by transferring 250g of tissue to the bulk archive sample container, thus ensuring that at least one large volume (bulk) aliquot is archived. Continue by transferring one 50g aliquot to a small archive container. Seal and label the containers as described in Step 17 for the other aliquots.

Any tissue that remains after filling the second bulk archive jar may be discarded.

Equipment Cleaning between Composite Samples

19. All of the homogenization equipment must be thoroughly cleaned between each composite sample. Once all of the fillets from the individual specimens in a given composite sample have been homogenized, disassemble the homogenization equipment (i.e., blender, grinder, or other device) and thoroughly clean all surfaces and parts that contact the sample. Similarly, clean all knives, cutting boards, and other utensils used. At a minimum:
    a. Wash with a detergent solution (phosphate- and scent-free) and warm tap water
    b. Rinse three times with warm tap water
    c. Rinse three times with deionized (DI) water
    d. Rinse with acetone
    e. Rinse three times with DI water
    f. Rinse with (not soak in) 5% nitric acid
    g. Rinse three times with DI water
    h. Allow the components to air dry
20. Reassemble the homogenization equipment and proceed with homogenization of the next sample in the batch (e.g., begin with Step 5 above).

Quality Control (QC) Procedures

The project-specific QC procedures include preparation and testing of equipment rinsate samples. The sample preparation laboratory will prepare one set of rinsate samples as described in Steps 21 - 22, below from the first composite processed. The rinsate results will be reviewed by the Tetra Tech PM and the NNEPA PM. Sample processing is dependent on both the quality of the sample preparation laboratory's efforts and on the timeliness of their delivery of QC results.

Rinsate and Blank Sample Production

21. Prior to reassembling the homogenization equipment (Step 20), prepare the rinsate sample, as follows:
    a. Prepare a DI water rinsate using 250 mL of DI water. Collect the DI water rinsate in a plastic 250ml bottle with nitric acid provided by the analytical laboratory. Place a second aliquot of DI water in a separate similar clean container for use as a blank.

Note: In order to minimize the number of project samples that might be affected by cross contamination, collect the rinsate samples on the first day of processing.

22. Label each container as either "rinsate" or "blank" and include the date it was prepared (mm/dd/yyyy). Store the rinsate and blank cold (<6°C).

Corrective Actions for Rinsates

The Tetra Tech PM will evaluate the rinsate results based on the mass of each analyte detected, and assuming that all of the apparent contamination could be transferred to a nominal 20-g mass of homogenized tissue. Results above the anticipated reporting limits for the analytes in tissue samples may be cause for corrective actions by the sample preparation laboratory. Such corrective actions may include revisions to the sample preparation laboratory's equipment cleaning procedures, followed by a successful demonstration of the revised cleaning procedures through preparation and analysis of additional rinsate samples.

Reporting Requirements

23. The sample preparation laboratory will prepare a weekly progress report to document the status of fish preparation activities and deliver the report electronically to the Tetra Tech PM. The weekly progress report will be delivered as an Excel spreadsheet. For each fillet composite, include at least the following information in the report:
    - site identification number,
    - sample identification number,
    - specimen numbers of the fish homogenized for the fillet composite,
    - common name for the fish species,
    - field-determined lengths and lab-determined weights of individual specimens,
    - total composite sample (i.e., homogenate) weight (to the nearest gram),
    - analysis type (e.g., mercury),
    - aliquot weight (to the nearest 0.5 gram),

- preparation date (e.g., mm/dd/yyyy),
- QC sample identifiers, and
- airbill numbers for all sample shipments that week (these may include samples prepared during previous weeks), even though this information was transmitted to the Tetra Tech PM at the time of shipment.

The weekly report will be due by COB Monday, and will document sample preparation progress for the previous week.

Shipping Samples

24. No samples may be shipped to the analytical laboratory until the Tetra Tech PM and the NNEPA PM have reviewed the rinsate results. The Tetra Tech PM will notify the sample preparation laboratory by email when specific samples may be shipped to the analytical laboratory.
25. When shipping batches of pre-frozen fillet tissue aliquots, keep the individual containers bagged in the food-grade plastic freezer bags. Place these bags in a cooler with adequate space for the tissue containers, packing materials, and dry ice. Secure each of the tissue containers with packing materials (e.g., bubble wrap or foam) before adding the dry ice. Place a layer of newspaper on top of the containers before adding the dry ice, as this can prevent cracking the lids.

Note: The amount of dry ice required for shipping will depend on the number of jars in the cooler and the time of year. It should be an adequate supply to keep the tissue samples frozen for 48 hours (i.e., a minimum of 25 pounds of dry ice per cooler).

26. Record the samples contained in the cooler on a shipping form provided by the Tetra Tech PM and place the form in a plastic bag taped to the inside lid of the cooler. Secure the outside of the cooler with sealing tape, address it to the analytical laboratory, and attach a dry ice (dangerous goods) label. Ship the cooler via FedEx on a date that will allow delivery of the cooler to the analytical laboratory on a normal business day (e.g., no Saturday deliveries and no deliveries on U.S. Federal holidays without express permission from the Tetra Tech PM). Provide the air bill number for each shipment to the Tetra Tech PM via email on the day that the shipment occurs.

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Appendix B

Analytical Methods

METHOD 6020A

INDUCTIVELY COUPLED PLASMA - MASS SPECTROMETRY

1.0 SCOPE AND APPLICATION

1.1 Inductively coupled plasma-mass spectrometry (ICP-MS) is applicable to the determination of sub-µg/L concentrations of a large number of elements in water samples and in waste extracts or digests (References 1 and 2). When dissolved constituents are required, samples must be filtered and acid-preserved prior to analysis. No digestion is required prior to analysis for dissolved elements in water samples. Acid digestion prior to filtration and analysis is required for groundwater, aqueous samples, industrial wastes, soils, sludges, sediments, and other solid wastes for which total (acid-leachable) elements are required.

1.2 ICP-MS has been applied to the determination of over 60 elements in various matrices. Analytes for which EPA has demonstrated the acceptability of Method 6020 in a multi-laboratory study on solid and aqueous wastes are listed below.

Element		CASRN[a]
Aluminum	(Al)	7429-90-5
Antimony	(Sb)	7440-36-0
Arsenic	(As)	7440-38-2
Barium	(Ba)	7440-39-3
Beryllium	(Be)	7440-41-7
Cadmium	(Cd)	7440-43-9
Calcium	(Ca)	7440-70-2
Chromium	(Cr)	7440-47-3
Cobalt	(Co)	7440-48-4
Copper	(Cu)	7440-50-8
Iron	(Fe)	7439-89-6
Lead	(Pb)	7439-92-1
Magnesium	(Mg)	7439-95-4
Manganese	(Mn)	7439-96-5
Mercury	(Hg)	7439-97-6
Nickel	(Ni)	7440-02-0
Potassium	(K)	7440-09-7
Selenium	(Se)	7782-49-2
Sliver	(Ag)	7440-22-4
Sodium	(Na)	7440-23-5
Thallium	(Tl)	7440-28-0
Vanadium	(V)	7440-62-2
Zinc	(Zn)	7440-66-6

[a]Chemical Abstract Service Registry Number

Acceptability of the method for an element was based upon the multi-laboratory performance compared with that of either furnace atomic absorption spectrophotometry or inductively coupled plasma-atomic emission spectrometry. It should be noted that one multi-laboratory study was conducted in 1988 and advances in ICP-MS instrumentation and software have been made since that time and additional studies have been added with validation and improvements in performance of the method. Performance, in general, exceeds the multi-laboratory performance data for the listed elements. It is expected that current performance will exceed the multi-laboratory performance data for the listed elements (and others) that are provided in Section 13.0. Instrument detection limits, sensitivities, and linear ranges will vary with the matrices, instrumentation, and operating conditions. In relatively simple matrices, detection limits will generally be below 0.1 µg/L. Less sensitive elements (like Se and As) and desensitized major elements may be 1.0 µg/L or higher.

1.3 If Method 6020 is used to determine any analyte not listed in Section 1.2, it is the responsibility of the analyst to demonstrate the accuracy and precision of the method in the waste to be analyzed. The analyst is always required to monitor potential sources of interferences and take appropriate action to ensure data of known quality (see Section 9.4). Other elements and matrices may be analyzed by this method if performance is demonstrated for the analyte of interest, in the matrices of interest, at the concentration levels of interest in the same manner as the listed elements and matrices (see Sec. 9.0).

1.4 Use of this method should be relegated to spectroscopists who are knowledgeable in the recognition and in the correction of spectral, chemical, and physical interferences in ICP-MS.

1.5 An appropriate internal standard is required for each analyte determined by ICP-MS. Recommended internal standards are ^{6}Li, ^{45}Sc, ^{89}Y, ^{103}Rh, ^{115}In, ^{159}Tb, ^{165}Ho, and ^{209}Bi. The lithium internal standard should have an enriched abundance of ^{6}Li, so that interference from lithium native to the sample is minimized. Other elements may need to be used as internal standards when samples contain significant native amounts of the recommended internal standards.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis, samples which require total ("acid-leachable") values must be digested using appropriate sample preparation methods (such as Methods 3005 - 3052).

2.2 Method 6020 describes the multi-elemental determination of analytes by ICP-MS in environmental samples. The method measures ions produced by a radio-frequency inductively coupled plasma. Analyte species originating in a liquid are nebulized and the resulting aerosol is transported by argon gas into the plasma torch. The ions produced by high temperatures are entrained in the plasma gas and introduced, by means of an interface, into a mass spectrometer. The ions produced in the plasma are sorted according to their mass-to-charge ratios and quantified with a channel electron multiplier. Interferences must be assessed and valid corrections applied or the data flagged to indicate problems. Interference correction must include compensation for background ions contributed by the plasma gas, reagents, and constituents of the sample matrix.

3.0 DEFINITIONS

Refer to Chapter One and Chapter Three for a listing of applicable definitions.

4.0 INTERFERENCES

4.1 Isobaric elemental interferences in ICP-MS are caused by isotopes of different elements forming atomic ions with the same nominal mass-to-charge ratio (m/z). A data system must be used to correct for these interferences. This involves determining the signal for another isotope of the interfering element and subtracting the appropriate signal from the analyte isotope signal. Since commercial ICP-MS instruments nominally provide unit resolution at 10% of the peak height, very high ion currents at adjacent masses can also contribute to ion signals at the mass of interest. Although this type of interference is uncommon, it is not easily corrected, and samples exhibiting a significant problem of this type could require resolution improvement, matrix separation, or analysis using another verified and documented isotope, or use of another method.

4.2 Isobaric molecular and doubly-charged ion interferences in ICP-MS are caused by ions consisting of more than one atom or charge, respectively. Most isobaric interferences that could affect ICP-MS determinations have been identified in the literature (References 3 and 4). Examples include $^{75}ArCl^+$ ion on the ^{75}As signal and MoO^+ ions on the cadmium isotopes. While the approach used to correct for molecular isobaric interferences is demonstrated below using the natural isotope abundances from the literature (Reference 5), the most precise coefficients for an instrument can be determined from the ratio of the net isotope signals observed for a standard solution at a concentration providing suitable (<1 percent) counting statistics. Because the ^{35}Cl natural abundance of 75.77 percent is 3.13 times the ^{37}Cl abundance of 24.23 percent, the chloride correction for arsenic can be calculated (approximately) as follows (where the $^{38}Ar^{37}Cl^+$ contribution at m/z 75 is a negligible 0.06 percent of the $^{40}Ar^{35}Cl^+$ signal):

Corrected arsenic signal (using natural isotopes abundances for coefficient approximations) =
(m/z 75 signal) - (3.13) (m/z 77 signal) + (2.73) (m/z 82 signal),

where the final term adjusts for any selenium contribution at 77 m/z,

NOTE: Arsenic values can be biased high by this type of equation when the net signal at m/z 82 is caused by ions other than $^{82}Se^+$, (e.g., $^{81}BrH^+$ from bromine wastes [Reference 6]).

Similarly,

Corrected cadmium signal (using natural isotopes abundances for coefficient approximations) =
(m/z 114 signal) - (0.027)(m/z 118 signal) - (1.63)(m/z 108 signal),

where last 2 terms adjust for any $^{114Sn+}$ or $^{114}MoO^+$ contributions at m/z 114.

NOTE: Cadmium values will be biased low by this type of equation when $^{92}ZrO^+$ ions contribute at m/z 108, but use of m/z 111 for Cd is even subject to direct ($^{94}ZrOH^+$) and indirect ($^{90}ZrO^+$) additive interferences when Zr is present.

NOTE: As for the arsenic equation above, the coefficients could be improved. The most appropriate coefficients for a particular instrument can be determined from the ratio of the net isotope signals observed for a standard solution at a concentration providing suitable (<1 percent) counting precision.

The accuracy of these types of equations is based upon the constancy of the OBSERVED isotopic ratios for the interfering species. Corrections that presume a constant fraction of a molecular ion relative

to the "parent" ion have not been found (Ref. 7) to be reliable, e.g., oxide levels can vary with operating conditions. If a correction for an oxide ion is based upon the ratio of parent-to-oxide ion intensities, the correction must be adjusted for the degree of oxide formation by the use of an appropriate oxide internal standard previously demonstrated to form a similar level of oxide as the interferent. For example, this type of correction has been reported (Ref. 7) for oxide-ion corrections using ThO^+/Th^+ for the determination of rare earth elements. The use of aerosol desolvation and/or mixed gas plasmas have been shown to greatly reduce molecular interferences (Ref. 8). These techniques can be used provided that method detection limits, accuracy, and precision requirements for analysis of the samples can be met.

4.3 Additionally, solid phase chelation may be used to eliminate isobaric interferences from both element and molecular sources. An on-line method has been demonstrated for environmental waters such as sea water, drinking water and acid decomposed samples. Acid decomposed samples refer to samples decomposed by methods similar to methods 3052, 3051, 3050 or 3015. Samples with percent levels of iron and aluminum should be avoided. The method also provides a method for preconcentration to enhance detection limits simultaneously with

elimination of isobaric interferences. The method relies on chelating resins such as imminodiacetate or other appropriate resins and selectively concentrates the elements of interest while eliminating interfering elements from the sample matrix. By eliminating the elements that are direct isobaric interferences or those that form isobaric interfering molecular masses, the mass region is simplified and these interferences can not occur. The method has been proven effective for the certification of standard reference materials and validated using SRMs (References 13-15). The method has the potential to be used on-line or off-line as an effective sample preparation method specifically designed to address interference problems.

4.4 Physical interferences are associated with the sample nebulization and transport processes as well as with ion-transmission efficiencies. Nebulization and transport processes can be affected if a matrix component causes a change in surface tension or viscosity. Changes in matrix composition can cause significant signal suppression or enhancement (Ref. 9). Dissolved solids can deposit on the nebulizer tip of a pneumatic nebulizer and on the interface skimmers (reducing the orifice size and the instrument performance). Total solid levels below 0.2% (2,000 mg/L) have been currently recommended (Ref. 10) to minimize solid deposition. An internal standard can be used to correct for physical interferences, if it is carefully matched to the analyte so that the two elements are similarly affected by matrix changes (Ref. 11). When intolerable physical interferences are present in a sample, a significant suppression of the internal standard signals (to less than 30 % of the signals in the calibrations standard) will be observed. Dilution of the sample fivefold (1+4) will usually eliminate the problem (see Sec. 9.3).

4.5 Memory interferences or carry-over can occur when there are large concentration

differences between samples or standards which are analyzed sequentially. Sample deposition on the sampler and skimmer cones, spray chamber design, and the type of nebulizer affect the extent of the memory interferences which are observed. The rinse period between samples must be long enough to eliminate significant memory interference.

5.0 SAFETY

Refer to Chapter Three for a discussion on safety related references and issues.

6.0 EQUIPMENT AND SUPPLIES

6.1 Inductively coupled plasma-mass spectrometer:

6.1.1 A system capable of providing resolution, better than or equal to 1.0 amu at 10% peak height is required. The system must have a mass range from at least 6 to 240 amu and a data system that allows corrections for isobaric interferences and the application of the internal standard technique. Use of a mass-flow controller for the nebulizer argon and a peristaltic pump for the sample solution are recommended.

6.1.2 Argon gas supply: high-purity grade (99.99%).

7.0 REAGENTS AND STANDARDS

7.1 Acids used in the preparation of standards and for sample processing must be of high purity. Redistilled acids are recommended because of the high sensitivity of ICP-MS. Nitric acid at less than 2 per cent (v/v) is required for ICP-MS to minimize damage to the interface and to minimize isobaric molecular-ion interferences with the analytes. Many more molecular-ion interferences are observed when hydrochloric and sulfuric acids are used (References 3 and 4). Concentrations of antimony and silver between 50-500 µg/L require 1% (v/v) HCl for stability; for concentrations above 500 µg/L Ag, additional HCl will be needed. Consequently, accuracy of analytes requiring significant chloride molecular ion corrections (such as As and V) will degrade.

7.2 Reagent water: All references to water in the method refer to reagent water unless otherwise specified. Refer to Chapter One for a definition of reagent water.

7.3 Standard stock solutions for each analyte may be purchased or prepared from ultra-high purity grade chemicals or metals (99.99 or greater purity). See Method 6010 for instructions on preparing standard solutions from solids.

7.3.1 Bismuth internal standard stock solution (1 mL = 100 µg Bi): Dissolve 0.1115 g $_{Bi2O3}$ in a minimum amount of dilute HNO_3. Add 10 mL conc. HNO_3 and dilute to 1,000 mL with reagent water.

7.3.2 Holmium internal standard stock solution (1 mL = 100 µg Ho): Dissolve 0.1757 g $Ho_2(CO_3)_2@5H_2O$ in 10 mL reagent water and 10 mL HNO_3. After dissolution is complete, warm the solution to degas. Add 10 mL conc. HNO_3 and dilute to 1,000 mL with reagent water.

7.3.3 Indium internal standard stock solution (1 mL = 100 µg In): Dissolve 0.1000 g indium metal in 10 mL conc. HNO_3. Dilute to 1,000 mL with reagent water.

7.3.4 Lithium internal standard stock solution (1 mL = 100 µg ^6Li): Dissolve 0.6312 g 95-atom-% ^6Li, Li_2CO_3 in 10 mL of reagent water and 10 mL HNO_3. After dissolution is complete, warm the solution to degas. Add 10 mL conc. HNO_3 and dilute to 1,000 mL with reagent water.

7.3.5 Rhodium internal standard stock solution (1 mL = 100 µg Rh): Dissolve 0.3593 g ammonium hexachlororhodate (III) $(NH_4)_3RhCl_6$ in 10 mL reagent water. Add 100 mL conc. HCl and dilute to 1,000 mL with reagent water.

7.3.6 Scandium internal standard stock solution (1 mL = 100 µg Sc): Dissolve 0.15343 g Sc_2O_3 in 10 mL (1+1) hot HNO_3. Add 5 mL conc. HNO_3 and dilute to 1,000 mL with reagent water.

7.3.7 Terbium internal standard stock solution (1 mL = 100 µg Tb): Dissolve 0.1828 g $Tb_2(CO_3)_35H_2O$ in 10 mL (1+1) HNO_3. After dissolution is complete, warm the solution to degas. Add 5 mL conc. HNO_3 and dilute to 1,000 mL with reagent water.

7.3.8 Yttrium internal standard stock solution (1 mL = 100 µg Y): Dissolve 0.2316 g $Y_2(CO_3)_33H_2O$ in 10 mL (1+1) HNO_3. Add 5 mL conc. HNO_3 and dilute to 1,000 mL with reagent water.

7.3.9 Titanium interference stock solution (1 mL = 100 µg Ti): Dissolve 0.4133 g $(NH_4)_2TiF_6$ in reagent water. Add 2 drops conc. HF and dilute to 1,000 mL with reagent water.

7.3.10 Molybdenum interference stock solution (1 mL = 100 µg Mo): Dissolve 0.2043 g $(NH_4)_2MoO_4$ in reagent water. Dilute to 1,000 mL with reagent water.

7.3.11 Gold preservative stock solution for mercury (1 mL = 100 µg): Recommend purchasing as high purity prepared solution of $AuCl_3$ in dilute hydrochloric acid matrix.

7.4 Mixed calibration standard solutions are prepared by diluting the stock-standard solutions to levels in the linear range for the instrument in a solvent consisting of 1 percent (v/v) HNO_3 in reagent water. The calibration standard solutions must contain a suitable concentration of an appropriate internal standard for each analyte. Internal standards may be added on-line at the time of analysis using a second channel of the peristaltic pump and an appropriate mixing manifold. Generally, an internal standard should be no more than 50 amu removed from the analyte. Recommended internal standards include ^{6}Li, ^{45}Sc, ^{89}Y, ^{103}Rh, ^{115}In, ^{159}Tb, ^{169}Ho, and ^{209}Bi. Prior to preparing the mixed standards, each stock solution must be analyzed separately to determine possible spectral interferences or the presence of impurities. Care must be taken when preparing the mixed standards that the elements are compatible and stable. Transfer the mixed standard solutions to freshly acid-cleaned FEP fluorocarbon bottles for storage. Fresh mixed standards must be prepared as needed with the realization that concentrations can change on aging. Calibration standards must be initially verified using a quality control standard (see Section 7.7).

7.5 Blanks: Three types of blanks are required for the analysis. The calibration blank is used in establishing the calibration curve. The preparation blank is used to monitor for possible contamination resulting from the sample preparation procedure. The rinse blank is used to flush the system between all samples and standards.

7.5.1 The calibration blank consists of the same concentration(s) of the same acid(s) used to prepare the final dilution of the calibrating solutions of the analytes [often 1 percent HNO_3 (v/v) in reagent water] along with the selected concentrations of internal standards such that there is an appropriate internal standard element for each of the analytes. Use of HCl for antimony and silver is cited in Section 7.1.

7.5.2 The preparation (or reagent) blank must be carried through the complete preparation procedure and contain the same volumes of reagents as the sample solutions.

7.5.3 The rinse blank consists of 1 to 2 percent HNO_3 (v/v) in reagent water. Prepare a sufficient quantity to flush the system between standards and samples. If mercury is to be analyzed, the rinse blank should also contain 2 µg/mL (ppm) $AuCl_3$ solution.

7.6 The interference check solution (ICS) is prepared to contain known concentrations of interfering elements that will demonstrate the magnitude of interferences and provide an adequate test of any corrections. Chloride in the ICS provides a means to evaluate software corrections for chloride-related interferences such as $^{35}Cl^{16}O^+$ on $^{51}V^+$ and $^{40}Ar^{35}Cl^+$ on $^{75}As^+$. Iron is used to demonstrate adequate resolution of the spectrometer for the determination of manganese. Molybdenum serves to indicate oxide effects on cadmium isotopes. The other components are present to evaluate the ability of the measurement system to correct for various molecular-ion isobaric interferences. The ICS is used to verify that the interference levels are corrected by the data system within quality control limits.

NOTE: The final ICS solution concentrations in Table 1 are intended to evaluate corrections for known interferences on only the analytes in Sec. 1.2. If Method 6020 is used to determine an element not listed in Sec. 1.2, it is the responsibility of the analyst to modify the ICS solutions, or prepare an alternative ICS solution, to allow adequate verification of correction of interferences on the unlisted element (see Section 9.4).

7.6.1 These solutions must be prepared from ultra-pure reagents. They can be obtained commercially or prepared by the following procedure.

7.6.1.1 Mixed ICS solution I may be prepared by adding 13.903 g $Al(NO_3)_3@9H_2O$, 2.498 g $CaCO_3$ (dried at 180 EC for 1 hour before weighing), 1.000 g Fe, 1.658 g MgO, 2.305 g Na_2CO_3, and 1.767 g $_{K2CO3}$ to 25 mL of reagent water. Slowly add 40 mL of (1+1) HNO_3. After dissolution is complete, warm the solution to degas. Cool and dilute to 1,000 mL with reagent water.

7.6.1.2 Mixed ICS solution II may be prepared by slowly adding 7.444 g 85 % H_3PO_4, 6.373 g 96% H_2SO_4, 40.024 g 37% HCl, and 10.664 g citric acid $C_6O_7H_8$

to 100 mL of reagent water. Dilute to 1,000 mL with reagent water.

7.6.1.3 Mixed ICS solution III may be prepared by adding 1.00 mL each of 100-µg/mL arsenic, cadmium, selenium, chromium, cobalt, copper, manganese, nickel, silver, vanadium, and zinc stock solutions to about 50 mL reagent water. Add 2.0 mL concentrated HNO_3, and dilute to 100.0 mL with reagent water.

7.6.1.4 Working ICS Solutions

7.6.1.4.1 ICS-A may be prepared by adding 10.0 mL of mixed ICS solution I (Sec. 7.6.1.1), 2.0 mL each of 100-µg/mL titanium stock solution (Sec. 7.3.9) and molybdenum stock solution (Sec. 7.3.10), and 5.0 mL of mixed ICS solution II (Sec. 7.6.1.2). Dilute to 100 mL with reagent water. ICS solution A must be prepared fresh weekly.

7.6.1.4.2 ICS-AB may be prepared by adding 10.0 mL of mixed ICS solution I (Sec. 7.6.1.1), 2.0 mL each of 100-µg/mL titanium stock solution (Sec. 7.3.9) and molybdenum stock solution (Sec. 7.3.10), 5.0 mL of mixed ICS solution II

(Sec. 7.6.1.2), and 2.0 mL of Mixed ICS solution III (Sec. 7.6.1.3). Dilute to 100 mL with reagent water. Although the ICS solution AB must be prepared fresh weekly, the analyst should be aware that the solution may precipitate silver more quickly.

7.7 The quality control standard is the initial calibration verification solution (ICV), which must be prepared in the same acid matrix as the calibration standards. This solution must be an independent standard near the midpoint of the linear range at a concentration other than that used for instrument calibration. An independent standard is defined as a standard composed of the analytes from a source different from those used in the standards for instrument calibration.

7.8 Mass spectrometer tuning solution. A solution containing elements representing all of the mass regions of interest (for example, 10 µg/L of Li, Co, In, and Tl) must be prepared to verify that the resolution and mass calibration of the instrument are within the required specifications (see Section 10.1). This solution is also used to verify that the instrument has reached thermal stability (see Section 11.4).

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Sample collection procedures should address the considerations described in Chapter Nine.

8.2 See the introductory material in Chapter Three, Inorganic Analytes, for information on sample handling, storage, holding times and preservation. Only polyethylene or fluorocarbon (TFE or PFA) containers are recommended for use in this method.

9.0 QUALITY CONTROL

9.1 All quality control data should be maintained and be available for easy reference or inspection.

9.2 Instrument detection limits (IDLs) in µg/L can be estimated by calculating the average of the standard deviations of three runs on three non-consecutive days from the analysis of a reagent blank solution with seven consecutive measurements per day. Each measurement must be performed as though it were a separate analytical sample (i.e., each measurement must be followed by a rinse and/or any other procedure normally performed between the analysis of separate samples). IDLs must be determined at least every three months and kept with the instrument log book. Refer to Chapter One for additional guidance.

9.3 The intensities of all internal standards must be monitored for every analysis. If the intensity of any internal standard in a sample falls below 30 percent of the intensity of that internal standard in the initial calibration standard, a significant matrix effect must be suspected. Under these conditions, the detection limit has degraded and the correction ability of the internal standardization technique becomes questionable. The following procedure is followed: First, make sure the instrument has not just drifted by observing the internal standard intensities in the nearest clean matrix (calibration blank, Section 7.5.1). If the low internal standard intensities are also seen in the nearest calibration

blank, terminate the analysis, correct the problem, recalibrate, verify the new calibration, and reanalyze the affected samples. If drift has not occurred, matrix effects need to be removed by dilution of the affected sample. The sample must be diluted fivefold (1+4) and reanalyzed with the addition of appropriate amounts of internal standards. If the first dilution does not eliminate the problem, this procedure must be repeated until the internal-standard intensities rise above the 30 percent limit. Reported results must be corrected for all dilutions.

9.4 To obtain analyte data of known quality, it is necessary to measure more than the analytes of interest in order to apply corrections or to determine whether interference corrections are necessary. For example, tungsten oxide moleculars can be very difficult to distinguish from mercury isotopes. If the concentrations of interference sources (such as C, Cl, Mo, Zr, W) are such that, at the correction factor, the analyte is less than the limit of quantification and the concentration of interferents are insignificant, then the data may go uncorrected. Note that monitoring the interference sources does not necessarily require monitoring the interferant itself, but that a molecular species may be monitored to indicate the presence of the interferent. When correction equations are used, all QC criteria must also be met. Extensive QC for interference corrections are required at all times. The monitored masses must include those elements whose hydrogen, oxygen, hydroxyl, chlorine, nitrogen, carbon and sulfur molecular ions could impact the analytes of interest. Unsuspected interferences may be detected by adding pure major matrix components to a sample to observe any impact on the analyte signals. When an interference source is present, the sample elements impacted must be flagged to indicate (a) the percentage interference correction applied to the data or (b) an uncorrected interference by virtue of the elemental equation used for quantitation. The isotope proportions for an element or molecular-ion cluster provide information useful for quality assurance.

> NOTE: Only isobaric elemental, molecular, and doubly charged interference corrections which use the observed isotopic-response ratios or parent-to-oxide ratios (provided an oxide internal standard is used as described in Section 4.2) for each instrument system are acceptable corrections for use in Method 6020.

9.5 Dilution test (serial dilution): If the analyte concentration is within the linear dynamic range of the instrument and sufficiently high (minimally, a factor of at least 100 times greater than the concentration in the reagent blank, refer to Section 7.5.2), an analysis of a fivefold (1+4) dilution must agree within ± 10% of the original determination. If not, an interference effect must be suspected. One dilution test must be included for each twenty samples (or less) of each matrix in a batch.

9.6 Post-digestion spike addition: An analyte spike added to a portion of a prepared sample, or its dilution, should be recovered to within 75 to 125 percent of the known value or within the laboratory derived acceptance criteria. The spike addition should be based on the indigenous concentration of each element of interest in the sample. If the spike is not recovered within the specified limits, the sample must be diluted and reanalyzed to compensate for the matrix effect. Results must agree to within 10% of the original determination. The use of a standard-addition analysis procedure may also be used to compensate for this effect (refer to Method 7000).

9.7 A laboratory control sample (LCS) should be analyzed for each analyte using the

same sample preparations, analytical methods and QA/QC procedures employed for the test samples. One LCS should be prepared and analyzed for each sample batch at a frequency of one LCS for each 20 samples or less.

9.8 Check the instrument calibration by analyzing appropriate quality control solutions as follows:

9.8.1 Check instrument calibration using a calibration blank (Section 7.5.1) and the initial calibration verification solution (Sections 7.7 and 11.6).

9.8.2 Verify calibration at a frequency of every 10 analytical samples with the instrument check standard (Section 7.6) and the calibration blank (Section 7.5.1). These solutions must also be analyzed for each analyte at the beginning of the analysis and after the last sample.

9.8.3 The results of the initial calibration verification solution and the instrument check standard must agree within ± 10% of the expected value. If not, terminate the analysis, correct the problem, and recalibrate the instrument. Any sample analyzed under an out-of-control calibration must be reanalyzed .

9.8.4 The results of the calibration blank must be less than 3 times the current IDL for each element. If this is not the case, the reason for the out-of-control condition must be found and corrected, and affected samples must be reanalyzed. If the laboratory consistently has concentrations greater than 3 times the IDL, the IDL may be indicative of an estimated IDL and should be re-evaluated.

9.9 Verify the magnitude of elemental and molecular-ion isobaric interferences and the adequacy of any corrections at the beginning of an analytical run or once every 12 hours, whichever is more frequent. Do this by analyzing the interference check solutions A and AB. The analyst should be aware that precipitation from solution AB may occur with some elements, specifically silver. Refer to Section 4.0 for a discussion on interferences and potential solutions to those interferences if additional guidance is needed.

9.10 Analyze one duplicate sample for every matrix in a batch at a frequency of one matrix duplicate for every 20 samples.

9.10.1 The relative percent difference (RPD) between duplicate determinations must be calculated as follows:

$$RPD = \frac{|D_1 - D_2|}{(D_1 + D_2)/2} \times 100$$

where:

RPD = relative percent difference.

D_1 = first sample value.

D_2 = second sample value (duplicate)

A control limit of 20% RPD should not be exceeded for analyte values greater than 100 times the instrumental detection limit. If this limit is exceeded, the reason for the out-of-control situation must be found and corrected, and any samples analyzed during the out-of-control condition must be reanalyzed.

9.11 Ultra-trace analysis requires the use of clean chemistry. Several suggestions for reduction on the analytical blank are provided in Chapter Three.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Conduct mass calibration and resolution checks in the mass regions of interest. The mass calibration and resolution parameters are required criteria which must be met prior to any samples being analyzed. If the mass calibration differs more than 0.1 amu from the true value, then the mass calibration must be adjusted to the correct value. The resolution must also be verified to be less than 0.9 amu full width at 10 percent peak height.

10.2 Calibrate the instrument for the analytes of interest (recommended isotopes for the analytes in Sec. 1.2 are provided in Table 2), using the calibration blank and at least a single initial calibration standard according to the instrument manufacturer's procedure. Flush the system with the rinse blank (Sec. 7.5.3) between each standard solution. Use the average of at least three integrations for both calibration and sample analyses.

> NOTE: Analysts have noted improved performance in calibration stability if the instrument is exposed to the interference check solution after cleaning sampler and skimmer cones. Improved performance is also realized if the instrument is allowed to rinse for 5 or 10 minutes before the calibration blank is run.

10.3 All masses which could affect data quality should be monitored to determine potential effects from matrix components on the analyte peaks. The recommended isotopes to be monitored are listed in Table 2.

10.4 Immediately after the calibration has been established, the calibration must be verified and documented for every analyte by the analysis of the calibration verification solution (Section 7.7). When measurements exceed ± 10% of the accepted value, the analyses must be terminated, the problem corrected, the instrument recalibrated, and the new calibration verified. Any samples analyzed under an out-of-control calibration must be reanalyzed. During the course of an analytical run, the instrument may be "resloped" or recalibrated to correct for instrument drift but resloping must not be used as an alternative to reanalyzing samples following an unacceptable QC sample, such as a CCV. A recalibration must then be followed immediately by a new analysis of a CCV and CCB before any further samples may be analyzed.

11.0 PROCEDURE

11.1 Solubilization and digestion procedures are presented in Chapter Three (e.g., Methods 3005 - 3052).

> NOTE: If mercury is to be analyzed, the digestion procedure must use mixed nitric and hydrochloric acids through all steps of the digestion. Mercury will be lost if the sample is digested when hydrochloric acid is not present. If it has not already been added to the sample as a preservative, Au should be added to give a final concentration of 2 mg/L (use

2.0 mL of 5.3.11 per 100 mL of sample) to preserve the mercury and to prevent it from plating out in the sample introduction system.

11.2 Initiate appropriate operating configuration of the instruments computer according to the instrument manufacturer's instructions.

11.3 Set up the instrument with the proper operating parameters according to the instrument manufacturer's instructions.

11.4 Operating conditions: The analyst should follow the instructions provided by the instrument manufacturer. Allow at least 30 minutes for the instrument to equilibrate before analyzing any samples. This must be verified by analyzing a tuning solution (Section 7.8) at least four times with relative standard deviations of < 5% for the analytes contained in the tuning solution.

NOTE: The instrument should have features that protect itself from high ion currents. If not, precautions must be taken to protect the detector from high ion currents. A channel electron multiplier or active film multiplier suffer from fatigue after being exposed to high ion currents. This fatigue can last from several seconds to hours depending on the extent of exposure. During this time period, response factors are constantly changing, which invalidates the calibration curve, causes instability, and invalidates sample analyses.

11.5 Calibrate the instrument following the procedure outlined in Section 10.0.

11.6 Flush the system with the rinse blank solution (Sec. 7.5.3) until the signal levels return to the DQO or method's levels of quantitation (usually about 30 seconds) before the analysis of each sample (see Section 10.3). Nebulize each sample until a steady-state signal is achieved (usually about 30 seconds) prior to collecting data. Analyze the calibration verification solution (Section 7.6) and the calibration blank (Section 7.5.1) at a frequency of at least once every 10 analytical samples. Flow-injection systems may be used as long as they can meet the performance criteria of this method.

11.7 Dilute and reanalyze samples that are more concentrated than the linear range for an analyte (or species needed for a correction) or measure an alternate but less-abundant isotope. The linearity at the alternate mass must be confirmed by appropriate calibration (see Sec. 10.2 and 10.4). Alternatively apply solid phase chelation chromatography to eliminate the matrix as described in Sec. 4.3.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 The quantitative values shall be reported in appropriate units, such as micrograms per liter (µg/L) for aqueous samples and milligrams per kilogram (mg/kg) for solid samples. If dilutions were performed, the appropriate corrections must be applied to the sample values.

12.1.1 If appropriate, or required, calculate results for solids on a dry-weight basis as follows:

(1) A separate determination of percent solids must be performed.

(2) The concentrations determined in the digest are to be reported on the basis of the dry weight of the sample.

$$\text{Concentration (dry weight)(mg/kg)} = \frac{C \times V}{W \times S}$$

Where,

C = Digest Concentration (mg/L)

V = Final volume in liters after sample preparation

W = Weight in kg of wet sample

$$S = \frac{\%\ \text{Solids}}{100}$$

Calculations must include appropriate interference corrections (see Section 4.2 for examples), internal-standard normalization, and the summation of signals at 206, 207, and 208 m/z for lead (to compensate for any differences in the abundances of these isotopes between samples and standards).

13.0 METHOD PERFORMANCE

13.1 In an EPA multi-laboratory study (Ref. 12), twelve laboratories applied the ICP-MS technique to both aqueous and solid samples. Table 3 summarizes the method performance data for aqueous samples. Performance data for solid samples are provided in Table 4.

13.2 Table 5 summarizes the method performance data for aqueous and sea water samples with interfering elements removed and samples preconcentrated prior to analysis. Table 6 summarizes the performance data for a simulated drinking water standard.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions consult *Less is Better: Laboratory Chemical management for Waste Reduction* available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St., N.W. Washington, D.C. 20036, (202) 872-4477.

15.0 WASTE MANAGEMENT

The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by

complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* available from the American Chemical Society at the address listed in Sec. 14.2.

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17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

The pages to follow contain Tables 1 through 7, and a flow diagram of the method procedure

TABLE 1

RECOMMENDED INTERFERENCE CHECK SAMPLE COMPONENTS AND CONCENTRATIONS

Solution	Solution A	Solution AB
Compone	Concentration (mg/L)	Concentration (mg/L)
Al	100.0	100.0
Ca	300.0	300.0
Fe	250.0	250.0
Mg	100.0	100.0
Na	250.0	250.0
P	100.0	100.0
K	100.0	100.0
S	100.0	100.0
C	200.0	200.0
Cl	2000.0	2000.0
Mo	2.0	2.0
Ti	2.0	2.0
As	0.0	0.100
Cd	0.0	0.100
Cr	0.0	0.200
Co	0.0	0.200
Cu	0.0	0.200
Mn	0.0	0.200
Hg	0.0	0.020
Ni	0.0	0.200
Se	0.0	0.100
Ag	0.0	0.050
V	0.0	0.200
Zn	0.0	0.100

TABLE 2

RECOMMENDED ISOTOPES FOR SELECTED ELEMENTS

Element of interest	Mass
Aluminum	**27**
Antimony	121, **123**
Arsenic	**75**
Barium	138, 137, 136, **135**, 134
Beryllium	**9**
Bismuth (IS)	209
Cadmium	**114**, 112, **111**, 110, 113, 116, 106
Calcium (I)	42, 43, **44**, 46, 48
Chlorine (I)	35, 37, (77, 82)[a]
Chromium	**52**, **53**, **50**, 54
Cobalt	**59**
Copper	**63**, **65**
Holmium (IS)	165
Indium (IS)	**115**, 113
Iron (I)	**56**, **54**, **57**, 58
Lanthanum (I)	139
Lead	**208**, **207**, **206**, 204
Lithium (IS)	6[b], 7
Magnesium (I)	24, **25**, **26**
Manganese	**55**
Mercury	202, **200**, 199, 201
Molybdenum (I)	98, 96, 92, **97**, 94, (108)[a]
Nickel	58, **60**, 62, **61**, 64
Potassium (I)	**39**
Rhodium (IS)	103
Scandium (IS)	45
Selenium	80, **78**, **82**, **76**, **77**, 74
Silver	**107**, **109**
Sodium (I)	**23**
Terbium (IS)	159
Thallium	**205**, 203
Vanadium	**51**, **50**
Tin (I)	120, **118**
Yttrium (IS)	89
Zinc	64, **66**, **68**, **67**, 70

NOTE: Method 6020 is recommended for only those analytes listed in Sec.1.2. Other elements are included in this table because they are potential interferents (labeled I) in the determination of recommended analytes, or because they are commonly used internal standards (labeled IS). Isotopes are listed in descending order of natural abundance. The most generally useful isotopes are underlined and in boldface, although certain matrices may require the use of alternative isotopes.

[a] These masses are also useful for interference correction (Section 4.2).

[b] Internal standard must be enriched in the ^{6}Li isotope. This minimizes interference from indigenous lithium.

TABLE 3

ICP-MS MULTI-LABORATORY PRECISION AND ACCURACY DATA FOR AQUEOUS SOLUTIONS

Element	Comparability[a] Range	%RSD Range	N[b]	S[c]
Aluminum	95 - 100	11 - 14	14 - 14	4
Antimony	d	5.0 - 7.6	16 - 16	3
Arsenic	97 - 114	7.1 - 48	12 - 14	4
Barium	91 - 99	4.3 - 9.0	16 - 16	5
Beryllium	103 - 107	8.6 - 14	13 - 14	3
Cadmium	98 - 102	4.6 - 7.2	18 - 20	3
Calcium	99 - 107	5.7 - 23	17 - 18	5
Chromium	95 - 105	13 - 27	16 - 18	4
Cobalt	101 - 104	8.2 - 8.5	18 - 18	3
Copper	85 - 101	6.1 - 27	17 - 18	5
Iron	91 - 900	11 - 150*	10 - 12	5
Lead	71 - 137	11 - 23	17 - 18	6
Magnesium	98 - 102	10 - 15	16 - 16	5
Manganese	95 - 101	8.8 - 15	18 - 18	4
Nickel	98 - 101	6.1 - 6.7	18 - 18	2
Potassium	101 - 114	9.9 - 19	11 - 12	5
Selenium	102 - 107	15 - 25	12 - 12	3
Silver	104 - 105	5.2 - 7.7	13 - 16	2
Sodium	82 - 104	24 - 43	9 - 10	5
Thallium	88 - 97	9.7 - 12	18 - 18	3
Vanadium	107 - 142	23 - 68	8 - 13	3
Zinc	93 - 102	6.8 - 17	16 - 18	5

Data obtained from reference 12.

[a] Comparability refers to the percent agreement of mean ICP-MS values to those of the reference technique (ICP-AES or GFAA).

[b] N is the range of the number of ICP-MS measurements where the analyte values exceed the limit of quantitation (3.3 times the average IDL value). A larger number gives a more reliable comparison. [c] S is the number of samples with results greater than the limit of quantitation. [d] No comparability values are provided for antimony because of evidence that the reference data is affected by an interference.

TABLE 4

ICP-MS MULTI-LABORATORY PRECISION AND ACCURACY DATA FOR SOLID MATRICES

Element	Comparability[a] Range	%RSD Range	N[b]	S[c]
Aluminum	83 - 101	11 - 39	13 - 14	7
Antimony	d	12 - 21	15 - 16	2
Arsenic	79 - 102	12 - 23	16 - 16	7
Barium	100 - 102	4.3 - 17	15 - 16	7
Beryllium	50 - 87	19 - 34	12 - 14	5
Cadmium	93 - 100	6.2 - 25	19 - 20	5
Calcium	95 - 109	4.1 - 27	15 - 17	7
Chromium	77 - 98	11 - 32	17 - 18	7
Cobalt	43 - 102	15 - 30	17 - 18	6
Copper	90 - 109	9.0 - 25	18 - 18	7
Iron	87 - 99	6.7 - 21	12 - 12	7
Lead	90 - 104	5.9 - 28	15 - 18	7
Magnesium	89 - 111	7.6 - 37	15 - 16	7
Manganese	80 - 108	11 - 40	16 - 18	7
Nickel	87 - 117	9.2 - 29	16 - 18	7
Potassium	97 - 137	11 - 62	10 - 12	5
Selenium	81	39	12	1
Silver	43 - 112	12 - 33	15 - 15	3
Sodium	100 - 146	14 - 77	8 - 10	5
Thallium	91	33	18	1
Vanadium	83 - 147	20 - 70	6 - 14	7
Zinc	84 - 124	14 - 42	18 - 18	7

Data obtained from reference 12.

a Comparability refers to the percent agreement of mean ICP-MS values to those of the reference technique.

b N is the range of the number of ICP-MS measurements where the analyte values exceed the limit of quantitation (3.3 times the average IDL value).

c S is the number of samples with results greater than the limit of quantitation.

d No comparability values are provided for antimony because of evidence that the reference data is affected by an interference.

TABLE 5

EXAMPLE METHOD PERFORMANCE DATA FOR AQUEOUS AND SEA WATER SAMPLES[A]
WITH INTERFERING ELEMENTS REMOVED
AND SAMPLES PRECONCENTRATED PRIOR TO ANALYSIS

ELEMENT	ISOTOPE	CONCENTRATION (ng/mL)[B]		
		9.0 mL	27.0 mL	CERTFIED
Manganese	55	1.8±0.05	1.9±0.2	1.99±0.15
Nickel	58	0.32±0.018	0.32±0.04	0.30±0.04
Cobalt	59	0.033±0.002	0.028±0.003	0.025±0.006
Copper	63	0.68±0.03	0.63±0.03	0.68±0.04
Zinc	64	1.6±0.05	1.8±0.15	1.97±0.12
Copper	65	0.67±0.03	0.6±0.05	0.68±0.04
Zinc	66	1.6±0.06	1.8±0.2	1.97±0.12
Cadmium	112	0.020±0.0015	0.019±0.0018	0.019±0.004
Cadmium	114	0.020±0.0009	0.019±0.002	0.019±0.004
Lead	206	0.013±0.0009	0.019±0.0011	0.019±0.006
Lead	207	0.014±0.0005	0.019±0.004	0.019±0.006
Lead	208	0.014±0.0006	0.019±0.002	0.019±0.006

Data obtained from Ref. 12.

[A] The dilution of the sea-water during the adjustment of pH produced 10 mL samples containing 9 mL of sea-water and 30 mL samples containing 27 mL of sea-water. Samples containing 9.0 mL of CASS-2, n=5; samples containing 27.0 mL of CASS-2, n=3.

[B] Concentration (ng/mL) ± 95% confidence limits.

These data are provided for guidance purposes only.

TABLE 6

ANALYSIS OF NIST SRM 1643b, TRACE METALS IN WATER[A]

ELEMENT	ISOTOPE	CONCENTRATION (ng/ml)[B] DETERMINED	CERTIFIED
Manganese	55	30±1.3	28±2
Nickel	58	50±2	49±3
Cobalt	59	27±1.3	26±1
Nickel	60	51±2	49±3
Copper	63	23±1.0	21.9±0.4
Zinc	64	67±1.4	66±2
Copper	65	22±0.9	21.9±0.4
Zinc	66	67±1.8	66±2
Cadmium	111	20±0.5	20±1
Cadmium	112	19.9±0.3	20±1
Cadmium	114	19.8±0.4	20±1
Lead	206	23±0.5	23.7±0.7
Lead	207	23.9±0.4	23.7±0.7
Lead	208	24.2±0.4	23.7±0.7

Data obtained from reference 12.

[A] 5.0 mL samples, n=5.

[B] Concentration (ng/mL) ± 95% confidence limits

TABLE 7

COMPARISON OF TOTAL MERCURY RESULTS IN HEAVILY CONTAMINATED SOILS

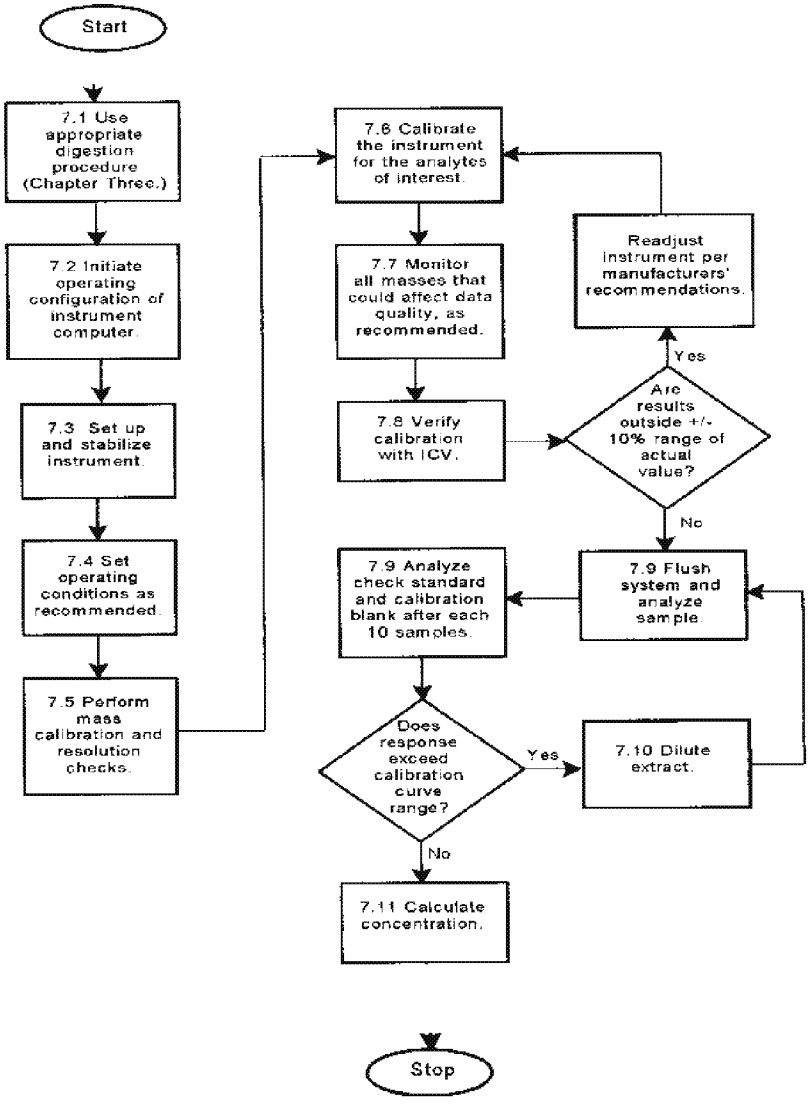
Soil Sample	Mercury in µg/g	
	ICP-MS	CVAA
1	27.8	29.2
2	442	376
3	64.7	58.2
4	339	589
5	281	454
6	23.8	21.4
7	217	183
8	157	129
9	1670	1360
10	73.5	64.8
11	2090	1830
12	96.4	85.8
13	1080	1190
14	294	258
15	3300	2850
16	301	281
17	2130	2020
18	247	226
19	2630	2080

Source: Reference 16.

METHOD 6020A

INDUCTIVERLY COUPLED PLASMA – MASS SPECTROMETRY

INDUCTIVELY COUPLED PLASMA - MASS SPECTROMETRY



METHOD 7471B

MERCURY IN SOLID OR SEMISOLID WASTE (MANUAL COLD-VAPOR TECHNIQUE)

SW-846 is not intended to be an analytical training manual. Therefore, method procedures are written based on the assumption that they will be performed by analysts who are formally trained in at least the basic principles of chemical analysis and in the use of the subject technology.

In addition, SW-846 methods, with the exception of required method use for the analysis of method-defined parameters, are intended to be guidance methods which contain general information on how to perform an analytical procedure or technique which a laboratory can use as a basic starting point for generating its own detailed Standard Operating Procedure (SOP), either for its own general use or for a specific project application. The performance data included in this method are for guidance purposes only, and are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

1.0 SCOPE AND APPLICATION

1.1 This method is a cold-vapor atomic absorption procedure for measuring the following RCRA analyte in soils, sediments, bottom deposits, and sludge-type materials:

Analyte	CAS Number*
Mercury, total (organic and inorganic)	7439-97-6

*Chemical Abstracts Registry Number

1.2 All samples must be subjected to an appropriate dissolution step prior to analysis. If this dissolution procedure is not sufficient to dissolve a specific matrix type or sample, then this method is not applicable for that matrix.

1.3 Prior to employing this method, analysts are advised to consult the disclaimer statement at the front of the manual and the information in Chapter Two for guidance on the intended flexibility in the choice of methods, apparatus, materials, reagents, and supplies, and on the responsibilities of the analyst for demonstrating that the techniques employed are appropriate for the analytes of interest, in the matrix of interest, and at the levels of concern.

In addition, analysts and data users are advised that, except where explicitly specified in a regulation, the use of SW-846 methods is *not* mandatory in response to Federal testing requirements. The information contained in this method is provided by EPA as guidance to be used by the analyst and the regulated community in making judgments necessary to generate results that meet the data quality objectives for the intended application.

1.4 Use of this method is restricted to use by, or under supervision of, properly experienced and trained personnel. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis, the solid or semi-solid samples must be prepared according to the procedures discussed in this method.

2.2 This method uses cold-vapor atomic absorption and is based on the absorption of radiation at the 253.7-nm wavelength by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration.

2.3 The typical instrument detection limit (IDL) for this method is 0.0002 mg/L.

3.0 DEFINITIONS

Refer to Chapter One, Chapter Three, and the manufacturer's instructions for definitions that may be relevant to this procedure.

4.0 INTERFERENCES

4.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be necessary. Refer to each method to be used for specific guidance on quality control procedures and to Chapter Three for general guidance on the cleaning of glassware. Also refer to Method 7000 for a discussion of interferences.

4.2 Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/Kg of sulfide, as sodium sulfide, do not interfere with the recovery of added inorganic mercury in reagent water.

4.3 Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/Kg had no effect on recovery of mercury from spiked samples.

4.4 Samples high in chlorides require additional permanganate (as much as 25 mL) because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation of 254 nm. Care must therefore be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 mL). In addition, the dead air space in the BOD bottle must be

purged before adding stannous sulfate. Alternatively, the sample may be allowed to stand for at least an hour under a hood (without active purging) to remove the chlorine.

4.5 Certain volatile organic materials that absorb at this wavelength may also cause interference. A preliminary run without reagents may be used to determine if this type of interference is present.

5.0 SAFETY

5.1 This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals listed in this method. A reference file of material safety data sheets (MSDSs) should be available to all personnel involved in these analyses.

5.2 Many mercury compounds are highly toxic if swallowed, inhaled, or absorbed through the skin. Extreme care must be exercised in the handling of concentrated mercury reagents. Concentrated mercury reagents should only be handled by analysts knowledgeable of their risks and of safe handling procedures.

6.0 EQUIPMENT AND SUPPLIES

The mention of trade names or commercial products in this manual is for illustrative purposes only, and does not constitute an EPA endorsement or exclusive recommendation for use. The products and instrument settings cited in SW-846 methods represent those products and settings used during method development or subsequently evaluated by the Agency. Glassware, reagents, supplies, equipment, and settings other than those listed in this manual may be employed provided that method performance appropriate for the intended application has been demonstrated and documented.

This section does not list common laboratory glassware (e.g., beakers and flasks).

6.1 Atomic absorption spectrophotometer or equivalent -- Any atomic absorption unit equipped with an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed. Instruments designed specifically for the measurement of mercury using the cold-vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

6.2 Mercury hollow cathode lamp or electrodeless discharge lamp.

6.3 Recording device -- Any multirange variable-speed recorder compatible equipped with the UV detection system or any other compatible data collection device.

6.4 Absorption cell -- Standard spectrophotometer cells 10 cm long equipped with

quartz end windows may be used. Suitable cells may be constructed from Plexiglas tubing, 1 in O.D. x 4.5 in. The ends are ground perpendicular to the longitudinal axis, and quartz windows (1 in diameter x 1/16 in thickness) are cemented in place. The cell is strapped to a burner for support and aligned in the light beam by use of two 2-in x 2-in cards. One inch diameter holes are cut in the middle of each card. The cards are then placed over each end of the cell. The cell is then positioned and adjusted vertically and horizontally to give the maximum transmittance.

6.5 Air pump -- Any peristaltic pump capable of delivering air at 1 L/min may be used. A Masterflex pump equipped with electronic speed control has been found to be satisfactory.

6.6 Flowmeter -- Capable of measuring an air flow of 1 L/min.

6.7 Aeration tubing -- A straight glass frit with a coarse porosity. Tygon tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell and return.

6.8 Drying tube -- 6-in x 3/4-in diameter tube containing 20 g of magnesium perchlorate or a small reading lamp, equipped with a 60-W bulb, which may be used to prevent condensation of moisture inside the cell. The lamp should be positioned to shine on the absorption cell so that the air temperature in the cell is about 10 °C above ambient.

6.9 The cold-vapor generator is assembled as shown in Figure 1 of Ref. 1 or according to the instrument manufacturer's instructions. The apparatus shown in Figure 1 of Ref. 1 is a closed system. An open system, where the mercury vapor is passed through the absorption cell only once, may be used instead of the closed system. Because mercury vapor is toxic, precaution must be taken to avoid its inhalation. Therefore, a bypass was included in the system either to vent the mercury vapor into an exhaust hood or to pass the vapor through some absorbing medium, such as:

1. Equal volumes of 0.1 M $KMnO_4$ and 10% H_2SO_4, or
2. Iodine 0.25% in a 3% KI solution.

A specially treated charcoal that will adsorb mercury vapor is also available from Barneby-Cheney, East 8th Avenue and North Cassidy Street, Columbus, Ohio 43219, Cat. #580-13 or #580-22.

6.10 Heating source -- Adjustable and capable of maintaining a temperature of 95 ± 3 °C. (e.g., hot plate, block digestor, microwave, etc.)

7.0 REAGENTS AND STANDARDS

7.1 Reagent-grade chemicals must be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 Reagent water -- Reagent water should be interference free. All references to water in this method refer to reagent water unless otherwise specified.

7.3 Aqua regia -- Prepare immediately before use by carefully adding three volumes of concentrated HCl to one volume of concentrated HNO_3.

7.4 Sulfuric acid, 0.5 N -- Dilute 14.0 mL of concentrated sulfuric acid to 1 L.

7.5 Stannous sulfate -- Add 25 g of stannous sulfate to 250 mL of 0.5 N sulfuric acid. This mixture is a suspension and should be stirred continuously during use. A 10% solution of stannous chloride (in water) can be substituted for the acidic stannous sulfate solution.

NOTE: If line clogging occurs when using an automated system, use a less concentrated stannous chloride solution.

7.6 Sodium chloride-hydroxylamine sulfate solution -- Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in reagent water and dilute to 100 mL. Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate. In this case, dissolve 12 g of hydroxylamine hydrochloride in reagent water and dilute to 100 mL.

7.7 Potassium permanganate, mercury-free, 5% solution (w/v) -- Dissolve 5 g of potassium permanganate in 100 mL of reagent water.

7.8 Mercury stock solution -- Dissolve 0.1354 g of mercuric chloride in 75 mL of reagent water. Add 10 mL of concentrated nitric acid and adjust the volume to 100.0 mL (1.0 mL = 1.0 mg Hg). Alternatively, a mercury stock solution may be purchased from a reputable source with a concentration of 1.0 mg Hg/mL. Verify the quality of the standard by checking it against a second source standard (see second paragraph of Sec. 9.4).

7.9 Mercury working standard -- Make successive dilutions of the stock mercury solution to obtain a working standard containing 0.1 πg/mL. This working standard and the dilution of the stock mercury solutions should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask, as needed, before adding the aliquot.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 See the introductory material to Chapter Three, "Inorganic Analytes."

8.2 All sample containers must be prewashed with detergents, acids, and reagent water. Glass, plastic, and polytetraflouroethylene (PTFE) containers are suitable in most cases. Polymers are not suitable for samples containing metallic mercury.

8.3 Metallic mercury, some inorganic mercury compounds, and many organic mercury

compounds are volatile and unstable. It is advantageous to analyze the samples as soon as possible to determine the total mercury in the sample but in no case exceed the 28-day limit as defined in Chapter Three of this manual. Non-aqueous samples must be analyzed as soon as possible. If solid samples are not analyzed immediately, refrigeration is necessary.

9.0 QUALITY CONTROL

9.1 Refer to Chapter One for additional guidance on quality assurance (QA) and quality control (QC) protocols. When inconsistencies exist between QC guidelines, method-specific QC criteria take precedence over both technique-specific criteria and those criteria given in Chapter One, and technique-specific QC criteria take precedence over the criteria in Chapter One. Any effort involving the collection of analytical data should include development of a structured and systematic planning document, such as a Quality Assurance Project Plan (QAPP) or a Sampling and Analysis Plan (SAP), which translates project objectives and specifications into directions for those that will implement the project and assess the results. Each laboratory should maintain a formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated. All data sheets and quality control data should be maintained for reference or inspection.

9.2 Initial demonstration of proficiency

Each laboratory must demonstrate initial proficiency by following the sample preparation and analytical procedures described in this method and generating data of acceptable accuracy and precision for the target analyte (Mercury) in a clean matrix. The laboratory must also repeat the demonstration of proficiency whenever new staff members are trained or significant changes in instrumentation are made.

9.3 For each batch of samples processed, at least one method blank must be carried throughout the entire sample preparation and analytical process. A method blank is prepared by using a volume or weight of reagent water at the volume or weight specified in the preparation method and then carried through the appropriate steps of the analytical process. These steps may include but are not limited to digestion, dilution, filtering, and analysis. If the method blank does not contain the target analyte at a level that interferes with the project-specific data quality objectives then the method blank would be considered acceptable. In the absence of project-specific data quality objectives, if the blank is less than the lower level of quantitation or less than 10% of the lowest sample concentration for the analyte, whichever is greater, then the method blank would be considered acceptable. If the method blank cannot be considered acceptable, the method blank should be re-run once and if still unacceptable then all samples after the last acceptable method blank must be reprepped and reanalyzed along with the other appropriate batch QC samples. These blanks will be useful in determining if samples are being contaminated.

9.4 For each batch of samples processed, at least one laboratory control sample must be carried throughout the entire sample preparation and analytical process. The laboratory control samples should be spiked with each analyte of interest at the project-specific action level or, when lacking project-specific action levels, between the low and midlevel standards. Acceptance criteria should be set at a laboratory derived limit developed through the use of historical analyses. In the absence of historical data this limit should be set at ± 20% of the

spiked value. After the determination of historical data, ± 20% should still be the limit of maximum deviation to express acceptability. If the laboratory control sample cannot be considered acceptable, the laboratory control sample should be re-run once and if still unacceptable then all samples after the last acceptable laboratory control sample must be reprepped and reanalyzed. Refer to Chapter One for more information.

If more than 10 samples per day are analyzed, the working standard curve must be verified by measuring satisfactorily a LCS or mid-range standard or reference standard after every 10 samples. This sample value should be within 20% of the true value, or the previous 10 samples must be reanalyzed.

9.5 Matrix spike/matrix spike duplicates (MS/MSDs) -- MS/MSDs are intralaboratory split samples spiked with identical concentrations of each analyte of interest. The spiking occurs prior to sample preparation and analysis. An MS/MSD is used to document the bias and precision of a method in a given sample matrix. Based on the analyst's discretion, a separate spike sample and a separate duplicate sample may be analyzed in lieu of the MS/MSD. For each batch of sample processed, at least one MS/MSD sample must be carried throughout the entire sample preparation and analytical process. MS/MSD samples should be spiked at the same level as the corresponding laboratory control sample that is at the project-specific action level or, when lacking project-specific action levels, between the low and midlevel standards. Acceptance criteria should be set at a laboratory derived limit developed through the use of historical analyses. In the absence of historical data this limit should be set at ± 20% of the spiked value for precision and ~ 20 relative percent difference (RPD). After the determination of historical data, 20% should still be the limit of maximum deviation for both percent recovery and relative percent difference to express acceptability.

9.6 The method of standard additions can be used to verify linearity or if matrix interference is suspected. Refer to Method 7000 for standard addition procedures.

9.7 Refer to Method 7000 for additional QA and QC information that may be applicable.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Standard preparation -- Transfer 0.0-, 0.5-, 1.0-, 2.0-, 5.0-, and 10-mL aliquots of the mercury working standard, containing 0-1.0 πg of mercury, to a series of 300-mL BOD bottles or equivalent. Add enough reagent water to each bottle to make a total volume of 10 mL. Add 5 mL of aqua regia and heat 2 min at 95 ± 3 °C. Allow the sample to cool; add 50 mL of reagent water and 15 mL of $KMnO_4$ solution to each bottle and heat again at 95 ± 3 °C for 30 min. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate. Add 50 mL of reagent water. Treating each bottle individually, add 5 mL of stannous sulfate solution, immediately attach the bottle to the aeration apparatus, and continue as described in Sec. 11.3.

10.2 Construct a calibration curve by plotting the absorbances of standards versus micrograms of mercury. Determine the peak height of the unknown from the chart or other recording device and read the mercury value from the standard curve.

11.0 PROCEDURE

11.1 Sample preparation

Weigh a 0.5 - 0.6 g-aliquot of a well homogenized sample and place in the bottom of a BOD bottle or other appropriate analysis vessel. Add 5 mL of reagent water and 5 mL of aqua regia. Heat 2 min at 95 ± 3 °C. Cool; then add 50 mL of reagent water and 15 mL of potassium permanganate solution to each sample and let stand at least 15 min. Add additional portions of permanganate solution, if needed, until the purple color persists for at least 15 min (see Sec. 4.4). Ensure that equal amounts of permanganate are added to standards and blanks. Mix thoroughly, then heat for 30 min at 95 ± 3 °C. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate to reduce the excess permanganate.

CAUTION: Do this addition under a hood, because Cl_2 could evolve. Add 55 mL of reagent water. Treating each bottle individually, add 5 mL of stannous sulfate and immediately attach the bottle to the aeration apparatus. Continue as described under Sec. 11.3.

See Sec. 10.1 for directions regarding standard preparation.

11.2 Alternate digestion procedure

An alternate digestion procedure employing an autoclave may also be used. In this procedure, 5 mL of concentrated H_2SO_4 and 2 mL of concentrated HNO_3 are added to the 0.5 - 0.6 g of sample. Add 5 mL of saturated $KMnO_4$ solution and cover the bottle with a piece of aluminum foil. The samples are autoclaved at 121 ± 3 °C and 15 lb for 15 min. Cool, dilute to a volume of 100 mL with reagent water, and add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate. Purge the dead air space and continue as described under Sec. 11.3. Refer to the caution statement in Sec. 11.1 for the proper protocol in reducing the excess permanganate solution and adding stannous sulfate.

11.3 Analysis

At this point, allow the sample to stand quietly without manual agitation. Allow the circulating pump, which was previously adjusted to a rate of 1 L/min, to run continuously. The absorbance, as exhibited either on the spectrophotometer or the recorder, will increase and reach maximum within 30 sec. As soon as the absorbance reading levels off (approximately 1 min), open the bypass valve and continue the aeration until the absorbance returns to its minimum value. Close the bypass valve, remove the fritted tubing from the BOD bottle, and continue the aeration. Because of instrument variation refer to the manufacturer's recommended operating conditions when using this method.

11.4 See Sec. 10.2 for directions regarding calibration curve construction.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 Results need to be reported in units commensurate with their intended use and all dilutions need to be taken into account when computing final results.

12.2 Calculate metal concentrations (1) by the method of standard additions, (2) from a calibration curve, or (3) directly from the instrument's concentration read-out. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 µg/g dry weight).

13.0 METHOD PERFORMANCE

13.1 Performance data and related information are provided in SW-846 methods only as examples and guidance. The data do not represent required performance criteria for users of the methods. Instead, performance criteria should be developed on a project-specific basis, and the laboratory should establish in-house QC performance criteria for the application of this method. These performance data are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

13.2 Precision and accuracy data are available in Method 245.5 of Methods for Chemical Analysis of Water and Wastes. These data are provided for guidance purposes only.

13.2 The data shown in Table 1 were obtained from records of State and contractor laboratories. The data are intended to show the precision of the combined sample preparation and analysis method. These data are provided for guidance purposes only.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions consult *Less is Better: Laboratory Chemical Management for Waste Reduction* available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St., N.W. Washington, D.C. 20036,

http://www.acs.org.

15.0 WASTE MANAGEMENT

The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on

waste management, consult *The Waste Management Manual for Laboratory Personnel* available from the American Chemical Society at the address listed in Sec. 14.2.

16.0 REFERENCES

1. U.S. EPA, "Method 245.5," Methods for Chemical Analysis of Water and Wastes, Pub. EPA-600/4-82-055, December 1982.

2. A. Gaskill, "Compilation and Evaluation of RCRA Method Performance Data," Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

The following pages contain the table referenced by this method

TABLE 1

EXAMPLE METHOD PERFORMANCE DATA

Sample Matrix	Preparation Method	Laboratory Replicates
Emission control dust	Not known	12, 12 µg/g
Wastewater treatment sludge	Not known	0.4, 0.28 µg/g

Data taken from Ref. 2

METHOD 7471B

MERCURY IN SOLID SEMISOLID WASTE (MANUAL COLD VAPOR TECHNIQUE)